

SOIL SCIENCE

VOLUME XVI

JULY-DECEMBER, 1923

RUTGERS COLLEGE
NEW BRUNSWICK, NEW JERSEY
U. S. A.

PUBLISHED BY
WILLIAMS & WILKINS COMPANY
BALTIMORE, MARYLAND

SOIL SCIENCE

A MONTHLY JOURNAL DEVOTED TO PROBLEMS
IN SOIL PHYSICS, SOIL CHEMISTRY AND
SOIL BIOLOGY

JACOB G. LIPMAN, Editor-in-Chief

Assistant Editors

CARL R. WOODWARD

CHARLES A. DOEHLERT

IN CONSULTATION WITH

- DR. F. J. ALWAY, Univ. of Minnesota.
PROF. C. BARTHEL, Centralanstalten för
Tors-, svävsendet på Jordbruksområdet,
Stockholm, Sweden.
DR. M. W. BEIJERINCK, Technische-Hooge-
school, Delft, Holland.
PROF. A. W. BLAIR, Rutgers College.
DR. P. E. BROWN, Iowa State College of
Agriculture.
ALBERT BRUNO, Ministry of Agriculture,
Paris, France.
DIRECTOR H. R. CHRISTENSEN, Statens Plant-
cavls-Laboratorium, Copenhagen, Den-
mark.
DR. H. J. CONN, N. Y. State Exp. Station.
PROF. DR. H. VON FEUERZEV, Centralanstal-
ten för Förskningsverket på Jordbruks-
området, Stockholm, Sweden.
DR. E. B. FRED, University of Wisconsin.
DR. J. E. GREAVES, Utah Agricultural Col-
lege.
DIRECTOR ALEX. GREGOIRE, Agricultural
Experiment Station, Gembloux, Belgium.
DR. R. GREIG-SMITH, Linnean Society,
Sydney, New South Wales.
DR. B. L. HARTWELL, Rhode Island Experi-
ment Station.
- DR. D. J. HISSINK, Agricultural Experiment
Station, Groningen, Holland.
DR. C. B. LIPMAN, Univ. of California.
DR. BURTON E. LIVINGSTON, Johns Hopkins
University, Baltimore, Md.
DR. F. LÖHNIS, U. S. Dept. of Agriculture.
DR. T. L. LYON, Cornell University.
DR. M. M. McCOOT, Michigan Agricultural
College.
DR. W. H. MACINTIRE, Tenn. Exp. Station.
DR. E. A. MITSCHERLICH, University of
Königsberg, Prussia.
PROF. C. A. MOIERS, Tenn. Exp. Station.
DR. THEO. REMY, Institut für Boden und
Pflanzenbaulehre, Bonn, Rh.
PROF. G. RUSSI, Royal Agricultural High
School in Portici, Naples, Italy.
DR. E. J. KUNST, Rothamsted Experi-
ment Station, Harpenden, England.
DR. O. SCHKLINER, U. S. Dept. of Agricul-
ture.
DR. ALIXIU, A. F. DE'SKIMOND, Royal Joseph
University of Technology, Budapest
Hungary.
PROF. CHAS. E. THORNTON, Ohio Experi-
ment Station.
PROF. N. M. TULAIKOV, A
periment Station, Saratov

SOIL SCIENCE, founded in 1916 by Rutgers College, the
State College for the Benefit of Agriculture and the Mechanic.
Published monthly by the Williams & Wilkins Company, Baltimore,

Second-Class Matter, August 23, 1918, at the Post Office at Baltimore, Maryland
Act of March 3, 1879.
Copyright 1924 by WILLIAMS & WILKINS COMPANY

CONTENTS

The Influence of Calcic and Magnesic Additions upon the Outgo of Sulfates from a Loam Soil as Measured by Lysimeter Leachings over an 8-year Period. W. H. MACINTIRE, W. M. SHAW AND J. B. YOUNG.....	1
Soil Acidity, an Ecological Factor. ARTHUR PIERSON KELLEY.....	41
Microbiological Analysis of Soil as an Index of Soil Fertility: VI. Nitrification. SELMAN A. WAKSMAN.....	55
Influence of Soil Moisture and Acidity on the Development of Potato Scab. WM. H. MARTIN.....	69
A Modification of the Truog Soil Acidity Test. F. W. PARKER AND J. W. TIDMORE.....	75
A Comparison of the Jones Calcium Acetate Method for Lime Requirement with the Hydrogen-Ion Concentration of Some Quebec Soils. EVERETT A. CARLETON.....	79
The Litmus Method for Detecting the Soil Reaction. EVERETT A. CARLETON.....	91
Soil Profile Studies in Michigan. M. M. MCCOOL, J. O. VEATCH AND C. H. SPURWAY.....	95
Comparative Effects of Muriate and Sulfate of Potash on the Soil in a Long Continued Fertilizer Experiment. F. W. MORSE.....	107
The Influence of the Nitrogen Treatment on the Content of Nitrogen, Carbon and Phosphoric Acid in a Soil Varying in Mechanical Composition. A. W. BLAIR AND A. L. PRINCE.....	115
Effect of Drying and Storage upon the Hydrogen-Ion Concentration of Soil Samples. CLAYTON O. ROST AND ERNEST A. FIEGER.....	121
Effect of Sulfur, Calcium and Phosphorus on the Yield and Composition of Alfalfa on Six Types of Idaho Soils. RAY E. NEIDIG, G. R. MCDOLE AND H. P. MAGNUSON.....	127
Partial Sterilization of Soil, Microbiological Activities and Soil Fertility: I. SELMAN A. WAKSMAN AND ROBERT L. STARKEY.....	137
Influence of Calcic and Magnesic Treatments upon Sulfate Leachings from Soil Alone and with Additions of Ferrous Sulfate, Pyrite, and Sulfur. W. H. MACINTIRE, W. M. SHAW, AND J. B. YOUNG.....	159
A Preliminary Study of the Effects of Sodium Chloride upon Alfalfa Grown in Solution Cultures. S. LOMANITZ.....	183
Acidity of Highly Basic Soils. W. T. McGEORGE.....	195
The Occurrence and Action of Fungi in Soils. ERNEST V. ABBOTT.....	207
A 5-Year Lysimeter Study of the Supposed Liberation of Soil Potassium by Calcic and Magnesic Additions. W. H. MACINTIRE, W. M. SHAW AND J. B. YOUNG.....	217
The Absorption of Ions by Plants. D. R. HOAGLAND.....	225
Partial Sterilization of Soil, Microbiological Activities and Soil Fertility: II. SELMAN A. WAKSMAN AND ROBERT L. STARKEY.....	247)
The Chlorosis of Pineapple Plants Grown on Manganiferous Soils. W. T. McGEORGE.....	269
The Effect of Moisture on Soil Color. A. M. O'NEAL.....	275
Organic Phosphorus of Soils. J. T. AUTEN.....	281
Equilibrium Studies of Sodium Carbonates and Bicarbonates in Some Idaho Soils. RAY E. NEIDIG AND HARRY P. MAGNUSON.....	295
The Variant Roles of Soil and Subsoil in Calcium-Magnesium Interchange. W. H. MACINTIRE, W. M. SHAW AND J. B. YOUNG.....	321
Partial Sterilization of Soil, Microbiological Activities and Soil Fertility: III. SELMAN A. WAKSMAN AND ROBERT L. STARKEY.....	343
Convenient Supports for Plants in Pot or Water Culture Experiments. J. S. MCHARGUE.	359

A New Apparatus for Mechanical Analysis of Soils.	HARLAN W. JOHNSON.....	363
A Comparison of Sand and Solution Cultures with Soils as Media for Plant Growth.	D. R. HOAGLAND AND J. C. MARTIN.....	367
The Liberation of Potassium from Feldspars, and of Potassium and Carbon Dioxide from Soils by Fertilizer and Acid Treatments.	S. C. VANDECAYE.....	389
The Leaching of Alkali Soil.	J. E. GREAVES, C. T. HIRST AND YEPPA LUND.....	407
The Effect of Plants on the Concentration of Drainage Water from the Cornell Lysimeters.	BENJAMIN D. WILSON.....	427
Studies on Virgin and Depleted Soils.	C. E. MILLAR.....	433
Reciprocal Repression Exerted by Calcic and Magnesian Additions upon the Solubility of Native Materials in Surface Soil.	W. H. MACINTIRE, W. M. SHAW, AND J. B. YOUNG.....	449
Comparison of the Soil Solution by Displacement Method and the Water Extract of Alkali Soils.	P. L. HIBBARD.....	465
The Hydrochloric Acid Method for Determining in the Soil the Cations present in an Absorbed Condition.	K. K. GEDROIZ.....	473
Soil Flora Studies.	THOMAS L. MARTIN.....	475
Studies on Sulfur Oxidation in Oregon Soils.	W. V. HALVERSEN AND W. B. BOLLEN....	479

ILLUSTRATIONS

PLATES

PARTIAL STERILIZATION OF SOIL, MICROBIOLOGICAL ACTIVITIES AND SOIL FERTILITY: I

- Plate 1. Influence of 1 per cent of Toluene upon the fungous flora of the soil..... 157

A PRELIMINARY STUDY OF THE EFFECTS OF SODIUM CHLORIDE UPON ALFALFA GROWN IN SOLUTION CULTURES

- Plate 1. Alfalfa nine weeks old, grown in solution cultures..... 193

THE EFFECT OF MOISTURE ON SOIL COLOR

- Plate 1. Fig. 1. Clinton silt loam. Fig. 2. Tama silt loam..... 279

CONVENIENT SUPPORTS FOR PLANTS IN POT OR WATER CULTURE EXPERIMENTS

- Plate 1. Method of supporting plants..... 361

TEXT-FIGURES

THE INFLUENCE OF CALCIC AND MAGNESIC ADDITIONS UPON THE OUTGO OF SULFATES FROM A LOAM SOIL AS MEASURED BY LYSIMETER LEACHINGS OVER AN 8-YEAR PERIOD

Fig. 1. Pounds of SO_3 per 2,000,000 pounds of soil in leachings from controls and silicate tanks.....	5
2. Pounds of SO_3 per 2,000,000 pounds of soil in leachings from tanks treated with CaO	8
3. Pounds of SO_3 per 2,000,000 pounds of soil in leachings from tanks treated with MgO equivalent to CaO	10
4. Pounds of SO_3 per 2,000,000 pounds of soil in leachings from tanks treated with CaCO_3 equivalent to CaO	12
5. Pounds of SO_3 per 2,000,000 pounds of soil in leachings from tanks treated with MgCO_3 equivalent to CaO	15
6. Pounds of SO_3 per 2,000,000 pounds of soil in leachings from tanks treated with limestone equivalent to CaO	19
7. Pounds of SO_3 per 2,000,000 pounds of soil in leachings from tanks treated with dolomite equivalent to CaO	26
8. Pounds of SO_3 per 2,000,000 pounds of soil in leachings from tanks treated with Magnesite Equivalent to CaO	31

SOIL ACIDITY, AN ECOLOGICAL FACTOR

Fig. 1. Graphs showing variation in acidity with depth.....	45
2. Root distribution in manor loam.....	49

MICROBIOLOGICAL ANALYSIS OF SOIL AS AN INDEX OF SOIL FERTILITY: VI.
NITRIFICATION

- Fig. 1. Influence of soil fertilization upon crop yield, numbers of microorganisms developing on the plate and nitrifying capacity of the soil. 64

A COMPARISON OF THE JONES CALCIUM ACETATE METHOD FOR LIME REQUIREMENT WITH THE HYDROGEN-ION CONCENTRATION OF SOME QUEBEC SOILS

- Fig. 1. Hydrogen Electrode and Vessel..... 82
 2. Soils arranged in order of increasing lime requirement and plotted for original reaction. Reaction after treatment, and lime requirement..... 88

PARTIAL STERILIZATION OF SOIL, MICROBIOLOGICAL ACTIVITIES AND SOIL FERTILITY: I

- Fig. 1. Influence of toluene and heat upon numbers of bacteria, fungi and accumulation of soluble nitrogen in an acid soil rich in organic matter (5A)..... 151
 2. Influence of toluene upon numbers of bacteria, fungi and accumulation of soluble nitrogen in an unlimed acid soil poor in organic matter (7A)..... 152
 3. Influence of toluene and heat upon numbers of bacteria, fungi and accumulation of soluble nitrogen in a limed, but slightly acid soil poor in organic matter (7B). 153

INFLUENCE OF CALCIC AND MAGNESIC TREATMENTS UPON SULFATE LEACHINGS FROM SOIL ALONE AND WITH ADDITIONS OF FERROUS SULFATE, PYRITE, AND SULFUR

- Fig. 1. Influence of CaO, MgO, limestone and dolomite upon leaching of sulfates derived from soil and rainfall and recovery of added FeSO₄, with and without CaO and MgO, as determined from periodic leachings over a 5-year interval..... 163
 2. Influence of CaO and MgO upon leachings of sulfates derived from pyrite and flowers of sulfur, as determined from periodic leachings over a 5-year interval.. 175

A PRELIMINARY STUDY OF THE EFFECTS OF SODIUM CHLORIDE UPON ALFALFA GROWN IN SOLUTION CULTURES

- Fig. 1. Graphs showing yields of tops, roots, and whole plants, relative to check taken as 100..... 187
 2. Graphs showing percentage of nitrogen in tops, roots and whole plants..... 188
 3. Graphs showing percentage of chlorine in tops, roots, and whole plants..... 188

A 5-YEAR LYSIMETER STUDY OF THE SUPPOSED LIBERATION OF SOIL POTASSIUM BY CALCIC AND MAGNESIC ADDITIONS

- Fig. 1. Increase or decrease in 5-year potassium outgo as caused by calcic and magnesic treatments of chemical equivalence..... 222

THE ABSORPTION OF IONS BY PLANTS

- Fig. 1. Absorption of ions from solutions of KNO₃ and Ca(NO₃)₂ of different concentrations..... 238
 2. Change of composition of complete culture solutions at various intervals over a period of 48 hours..... 241

PARTIAL STERILIZATION OF SOIL, MICROBIOLOGICAL ACTIVITIES AND SOIL
FERTILITY: II

Fig. 1. Course of biological activities in undisturbed soil.....	248
2. Influence of tillage on biological activities in soil.....	252
3. Influence of CaO on biological activities in soil.....	252
4. Influence of CaCO ₃ on biological activities in soil.....	254
5. Influence of air-drying and subsequent remoistening on biological activities in soil.....	255
6. Influence of air-drying, subsequent remoistening, and reinoculation on biological activities in soil.....	257
7. Influence of length of time a soil is air-dry upon its carbon-dioxide production upon being remoistened.....	257
8. Influence of heating on biological activities in soil.....	258
9. Influence of heating and reinoculation on biological activities in soil.....	260
10. Influence of toluene on biological activities in soil.....	262
11. Influence of toluene and reinoculation on biological activities in soil.....	262
12. Influence of CS ₂ on biological activities in soil.....	264
13. Influence of CS ₂ and reinoculation on biological activities in soil.....	264
14. Influence of organic matter on biological activities in soil.....	266
15. Influence of sulfur on biological activities in soil.....	266
16. Carbon-dioxide production effected by various treatments—Total CO ₂ produced during first week after treatment.....	267

EQUILIBRIUM STUDIES OF SODIUM CARBONATES AND BICARBONATES IN SOME IDAHO SOILS

Fig. 1. Curves representing sodium carbonate and sodium bicarbonate added to and recovered from palouse silt loam, when kept at a moisture content of 15 to 20 per cent.....	306
2. Curves representing sodium carbonate and sodium bicarbonate added to and recovered from Caldwell silt loam subsoil, when kept at a moisture content of 15 to 20 per cent.....	307
3. Curves representing sodium carbonate and sodium bicarbonate added to and recovered from Boise silt loam containing natural alkali chlorides and sulfates, when kept at a moisture content of 15 to 20 per cent.....	308
4. Curves representing sodium carbonate and sodium bicarbonate added to and recovered from Boise silt loam free from alkali chlorides and sulfates, when kept at a moisture content of 15 to 20 per cent.....	309
5. Diagram representing successive sodium carbonate and sodium bicarbonate treatments and respective salt recovery at the end of each series.....	313
6. Diagram representing successive sodium carbonate and sodium bicarbonate treatments and respective salt recovery at the end of each series.....	314

CONVENIENT SUPPORTS FOR PLANTS IN POTS AND WATER CULTURE EXPERIMENTS

Fig. 1. Method of making metal sockets for props.....	360
---	-----

A NEW APPARATUS FOR MECHANICAL ANALYSIS OF SOILS

Fig. 1. Curves showing actual points as located by balance.....	364
2. Curves of three soils not deflocculated.....	364
3. Curves of three soils deflocculated.....	364
4. Curves of two soils drawn as though recording mechanism were revolving twelve times as fast.....	364
8. Automatic recording balance arranged for making mechanical analyses of soils..	365

THE LIBERATION OF POTASSIUM FROM FELDSPARS, AND OF POTASSIUM AND CARBON DIOXIDE FROM SOILS BY FERTILIZER AND ACID TREATMENTS

- Fig. 1. Graph showing the effect of manure extract and acid treatments on solutions containing orthoclase and alumite..... 390
2. Graph showing average increase in water-soluble potassium and pH values of the different treatments after sixteen weeks..... 394
3. Graph showing the relation between the production of carbon dioxide and the liberation of water soluble potassium in sterile and non-sterile soils, and the relation of the pH value to the production of carbon dioxide, or the liberation of water-soluble potassium in the same soils..... 403

STUDIES ON SULFUR OXIDATION IN OREGON SOILS

- Fig. 1. Water-holding capacity and sulfur oxidation..... 485
2. Sulfur, sulfates and sulfur-oxidizing power..... 488

ERRATA

This errata slip is to replace that issued with **SOIL SCIENCE**, v. 15, no. 6, opposite page 427.

Pages 324-325. In columns 8 and 9 read Soil | Subsoil instead of "Soil 1." Units for both columns are *per cent*.

ERRATA

Vol. 16, p. 141, line 9: Read "A stream of air was passed through the bell-jars," etc.

Vol. 16, p. 156: Add to legend for Plate 1, "1 = 5 A, 2 = 7 A, 3 = 9 A, 4 = 11 A,
5 = 7 B."

ERRATA

p. 90, read: (10) Joffe, J. S. 1920, etc.

p. 385, last line, read: be called the "physiological soil solution," etc.

p. 386, 27th line, read: the weight of those produced in a good soil, etc.

THE INFLUENCE OF CALCIC AND MAGNESIC ADDITIONS UPON
THE OUTGO OF SULFATES FROM A LOAM SOIL AS MEAS-
URED BY LYSIMETER LEACHINGS OVER
AN 8-YEAR PERIOD

W. H. MACINTIRE, W. M. SHAW AND J. B. YOUNG¹

University of Tennessee Agricultural Experiment Station

Received for publication March 5, 1923

INTRODUCTORY

The subject of soluble soil sulfates is one of importance. Field lysimeters probably afford the best opportunity to study the occurrence of such salts, their availability under different conditions, and the progress of sulfification. The few available lysimeter data on sulfate leachings have been compiled by Lyon and Bizzell (2, p. 77) and will not be cited here. Unqualified application of such results is hardly permissible, since only those cited from Von Seelhorst were secured from experimentation extending beyond periods of a few months, which intervals we will show constitute the period of initial abnormality in sulfate outgo.

The results to be offered in this contribution constitute a study of the formation of sulfates and subsequent acceleration or retardation of leaching, as influenced by different forms and varying amounts of calcic and magnesic materials. The investigation also included a study of the balance between sulfur precipitation in rainfall and loss through leaching. The leachings were all from fallow soil, thus avoiding the influence of plant growth. The duplication of treatments in surface soil alone and in surface soil underlaid by subsoil afforded opportunity for determination of the function of the subsoil in changing the sulfate concentration of the leachings from the surface soil. In this regard the investigation may be considered as distinctive. In so far as we are aware, it is also without parallel in scope of comparisons and magnitude of treatments, nine different calcic and magnesic materials being used, with an upper limit of 100 tons of CaO, or its equivalent, per acre.

EXPERIMENTAL

The experimental results were obtained during an 8-year study with 46 field lysimeters each 1/20,000 acre in area. The experimental period ex-

¹ Much of the earlier analytical work in this investigation was done by Messrs. L. G. Willis, W. A. Holding and F. J. Gray, formerly of the Tennessee Agricultural Experiment Station.

tended from July 15, 1914, to July 15, 1922. The soil used is a Cumberland loam of the Hagerstown series and was obtained from a nearby source. It was so protected as to maintain a condition close to the optimum of moisture content throughout the processes of screening, mixing to insure uniformity and the working in of additions. Each tank received the equivalent of 100 pounds of moisture-free soil. The treatments were CaO, MgO, CaCO₃, MgCO₃, 100-mesh limestone, 100-mesh dolomite and 100-mesh magnesite, each at the *CaO equivalent* rate of 8 tons, 32 tons, and 100 tons per 2,000,000 pounds of soil. Wherever used in the text in connection with these seven treatments the three terms *8-ton*, *32-ton* and *100-ton* are intended to express

TABLE 1
Composition of soil and materials used for treatments

LABORATORY NUMBER	MATERIAL	SiO ₂	Fe ₂ O ₃ AND Al ₂ O ₃	CaO	MgO	CO ₂	CaCO ₃	MgCO ₃	SO ₃
		per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
3216	CaO.....	0.10	0.53	97.15§	0.87	0.13	0.30	0.00	0.00
3222	MgO.....	0.27	0.00	2.58	90.10	1.29	0.00	2.47	0.25
3220	CaCO ₃	0.18	0.00	54.93	0.38	43.09	98.09	0.80	0.26
3221	MgCO ₃ *.....	0.31	0.00	0.00	43.38	35.50	0.00	68.04	0.15
3217	Limestone.....	2.45	0.85	52.83	0.78	42.57	94.33	1.49	0.00
3218	Dolomite.....	9.66	1.00	27.98	18.70	40.98	49.96	35.70†	2.33
3219	Magnesite.....	1.94‡	0.28	0.00	47.53	50.45	0.00	96.68‡	0.14
3227	Wollastonite.....	45.11	0.48	0.69	1.57	0.00	0.06
3228	Serpentine.....	0.09	37.79	0.14	0.00	0.27	0.28
3343	Soil†.....	0.18	0.30	0.1060
3224	Subsoil†.....	0.19	0.47	0.0840

* Analysis calculates to formula, 3 MgCO₃ · Mg(OH)₂ · 3 H₂O plus 3.25 per cent moisture.

† Carbonate fusion.

‡ MgSiO₃, 3.24 per cent.

|| By difference.

¶ Most probably some MgSiO₃ present.

§ Contained 5.84 per cent Ca(OH)₂.

equivalence of CaO. The analyses of the calcic and magnesian materials are given in table 1. The primary object of the experiment was a study of alkali-earth absorption, hence, the range in treatments up to excessive amounts. The effect of treatments as low as one ton of CaO, or its equivalent, will be considered in another paper. All treatments were mixed throughout the entire amount of soil. Each treatment was made to a tank which had 8 inches of surface soil and no subsoil and also to a tank which contained the same amount of surface soil and one foot of red clay subsoil. The surface soil tanks will also be referred to as shallow tanks; the subsoil tanks, as deep tanks. In addition, one of the deep tanks received 100-mesh wollastonite at the rate of 32 tons per 2,000,000 pounds of soil and another received 100-

mesh serpentine at the same rate. Fitting in the original scheme, the two silicate tanks were included instead of no-treatment controls. The untreated controls 45 and 46 were installed after the second year. The average annual losses are therefore determined by division by 6 in the case of the controls and by 8 in the case of treatments. No addition of sulfur was made to any of the tanks, save as treatment impurities and that which was carried by the natural rainfall. The sulfate precipitations over the same 8-year period have been reported (7). A preliminary contribution (8) has been offered, showing the divergent effects of calcium and magnesium during the first two years of the 8-year period. The field lysimeter equipment has also been described (4, p. 6-8; 6). The analyses for sulfate outgo were made upon each of the eight annual composites, and are given in tables 3, 4 and 5. The sulfate determinations were all made gravimetrically, in duplicate, with a 2 mgm. analytical limit of variation. This analytical limit of error is equivalent to 3.8 pounds of SO_3 per acre per annum from a representative leaching of 125 liters per tank.

AMOUNTS OF SULFUR CONTAINED IN SOIL, TREATMENTS, AND RAINFALL

The amount of sulfur present in each of the several containers was not a constant, because of the variation in the sulfur carried by the different treatments and because of the several rates of addition. The subsoil tanks contained greater quantities of sulfur than the corresponding tanks which had only the surface soil. The SO_3 content of surface soil was found to be 0.1060 per cent and that of subsoil 0.0840 per cent. The total sulfur occurrences in soil and subsoil were obtained by oxidation with sodium peroxide. The studies leading to perfection of the method and the details of manipulation will be given in another contribution. A 3-hour agitation of 20-gm. charges in 150 cc. of water gave SO_3 occurrences of 0.0152 per cent and 0.0185 per cent for soil and subsoil, respectively. The earlier contribution on rainfall sulfur showed the abnormal precipitation over the 8-year period of experimentation to be practically one-half of that contained by the soil at the beginning of the experiment. The total sulfur supply of each tank, as represented by the composition of soil, subsoil, treatment-impurities, and the atmospheric precipitation, is given in table 2.

THE SULFATE CONTENT OF LEACHINGS

The sulfate losses from the additions of calcic and magnesic materials, as determined by the leaching analyses, will be considered under four headings:

- (1) *Comparison between treatments* in each 7-unit group with reference to the divergent effect of calcium and magnesium in materials of varying form and solubility and with variation in soil depth, without regard to source of sulfur.
- (2) *Effect of each separate material* as it may vary with the magnitude of addition and with soil depth, without consideration of the source of sulfur.

(3) *Comparison between treatments* in each 7-unit group as showing the relationships between (A) losses and the sulfur derived from each source and (B) losses and the aggregate of all sulfur supplies.

TABLE 2

Possible sources of sulfates in leachings. Amounts of SO₂ in loam soil, subsoil, alkali-earth treatments and in the 8-year precipitation

TREATMENT	SO ₂ IN SOIL		SULFATE IN 8 YEARS RAINFALL	SO ₂ AVAILABLE PER ACRE FROM SOIL CONSTANT, RAINFALL CONSTANT AND TREATMENT VARIABLE					
				8-ton treatment		32-ton treatment		100-ton treatment	
	Surface soil	Subsoil		As impurities in treatment	Total from all sources	As impurities in treatment	Total from all sources	As impurities in treatment	Total from all sources
	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
CaO.....	2120	1029	0	3149	0	3149	0	3149
CaO.....	2120	2772	1029	0	5921	0	5921	0	5921
MgO.....	2120	1029	30	3179	120	3269	375	3524
MgO.....	2120	2772	1029	30	5951	120	6041	375	6296
CaCO ₃	2120	1029	72	3221	288	3437	900	4049
CaCO ₃	2120	2772	1029	72	5993	288	6209	900	6821
MgCO ₃	2120	1029	37	3186	148	3297	463	3612
MgCO ₃	2120	2772	1029	37	5958	148	6069	463	6384
Limestone.....	2120	1029	0	3149	0	3149	0	3149
Limestone.....	2120	2772	1029	0	5921	0	5921	0	5921
Dolomite.....	2120	1029	701	3850	2804	5953	8763	11912
Dolomite.....	2120	2772	1029	701	6622	2804	8725	8763	14684
Magnesite.....	2120	1029	33	3182	132	3281	413	3562
Magnesite.....	2120	2772	1029	33	5954	132	6053	413	6334
Wollastonite.....	2120	2772	1029	40	5961†
Serpentine.....	2120	2772	1029	180	6101†
‡									
None.....	2120	772*
None 	2120	2772	772*

* Six years.

† Actual rate of 32 tons of material.

‡ Total, 2892 pounds.

|| Total, 5664 pounds.

(4) *Effect of such separate material* as showing the influence of rate of treatment and relation of sulfate outgo to each partial source and the total of all sulfur present.

EIGHT-TON TREATMENT

Surface-soil tanks

Increased outgo of sulfates from the surface soil was induced by all of the calcic and magnesic additions at the 8-ton rate during the initial year, as will be seen by reference in table 3. The outgo from each treatment was in excess of the water soluble sulfate content of the dry reserve sample. It is most probable that this increase was due chiefly to acceleration in bacterial activities, although it might be contended that the added materials served to reduce the soil's physical ability to retain sulfates. The minimum amount

1000

Figure 1

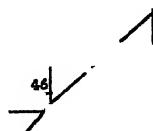
750500250

FIG. 1. POUNDS OF SO₃ PER 2,000,000 POUNDS OF SOIL IN LEACHINGS FROM CONTROLS AND SILICATE TANKS

- Tank 43—32 tons wollastonite, soil-subsoil
- 44—32 tons sepientine, soil-subsoil
- 45—control, soil-subsoil
- 46—control, surface soil only

of 341 pounds of SO₃ resulted from the burnt lime treatment and the maximum of 540 pounds, from the limestone addition. This maximum for the initial year was more than equivalent to the total outgo from the shallow-tank control for the 6-year period. The initial annual sulfate loss from both magnesium carbonate and magnesite was practically equivalent to the 6-year aggregate outgo from the control tank. Magnesium oxide proved more active than calcium oxide in accelerating the leaching of sulfates. The precipitated carbonate of magnesium was also more active than the corresponding form of calcium. As compared with the first year's results, there was a decided

TABLE 3
Sulfate content of leachings from loam soil with treatments equivalent to 8 tons CaO per acre

TREATMENT NUMBER	TREATMENT	AS TO SUBSOIL	TOTAL VOLUME OF LEACHINGS	SO ₂ LEACHED PER 2,000,000 POUNDS OF SOIL													
				First 4-year period				Second 4-year period				Annual average	Total				
				1st year	2d year	3rd year	4th year	5th year	6th year	7th year	8th year						
			liters	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.				
1	CaO.....	None	991	341	267	112	67	197	787	108	106	66	37	317	138	1104	
22	CaO.....	Clay	1060	33	68	197	101	100	399	166	229	132	66	148	593	124	992
2	MgO.....	None	979	469	141	119	67	199	796	100	119	67	36	81	322	140	1118
23	MgO.....	Clay	1021	40	162	269	126	149	597	153	215	130	55	138	553	144	1150
3	CaCO ₃	None	1009	468	203	140	87	225	898	108	111	68	37	81	324	153	1222
24	CaCO ₃	Clay	1073	35	58	222	82	99	397	253	280	138	65	184	736	142	1133
4	MgCO ₃	None	1076	528	170	102	63	216	863	100	110	79	37	82	326	149	1189
25	MgCO ₃	Clay	1011	32	136	330	113	153	611	163	203	115	54	134	535	143	1146
5	Limestone.....	None	1044	540	214	119	68	235	941	112	109	59	40	80	320	158	1261
26	Limestone.....	Clay	1024	20	29	190	82	80	321	153	239	149	69	153	610	116	931
6	Dolomite.....	None	950	402	215	130	101	212	848	139	134	99	51	106	423	159	1271
27	Dolomite.....	Clay	1024	21	27	92	54	49	194	134	224	162	79	150	599	99	793
7	Magnesite.....	None	1038	512	171	126	76	221	885	110	109	65	37	80	321	151	1206
28	Magnesite.....	Clay	973	31	36	99	52	55	218	136	244	152	65	149	597	102	815
46	None.....	None	838*	155	66	68	126	104	415	73	46	60	89	
45	None.....	Clay	777*	6	3	1	9	5	19	3	2	3	4	
	Inches of rainfall.....		47.78	56.54	63.32	47.79	51.41	54.21	50.37	55.63		

decrease in sulfates leached from all treatments during the second year and further progressive decreases during the third and fourth years. The initial 4-year totals show a minimum of 787 pounds for the CaO treatment and a maximum of 941 pounds for the limestone addition. The totals and average annual losses for the five carbonate treatments are grouped rather closely and are considerably greater than the corresponding results from the two oxide additions. As compared with the fourth year's results, leached sulfates increased somewhat during the fifth and sixth years. The losses for those two years are almost duplicated for each respective treatment, though the rainfall of the sixth year was considerably greater than that of the fifth. Again, during the seventh and eighth annual periods, there was a consistent decrease. This very definite tendency toward eventual decreases in sulfate outgo would naturally be expected to follow the depletion of the soil's native store of sulfur materials. The 8-year totals are in harmony with those of the first 4-year period in showing the two oxide tanks as trailing the remaining five carbonate treatments. The totals from the limestone and dolomite treatments are very close, that from the dolomite being the maximum outgo for the full 8-year period. The two precipitated carbonates come next in order, with rather close grouping.

Surface-soil and subsoil tanks

In contrast with the surface-soil tanks, those of the subsoil series yielded the smallest amount of sulfates during the initial year. During the second and third years a material increase is noted, especially in the case of the magnesium oxide and carbonate treatments, which induced a fourfold increase in outgo during the second year. The maximum annual loss of the first 4-year period was obtained from all seven treatments during the third year which was one of abnormal rainfall. Following the uniform drop of the fourth annual period every treatment gave an increase in the fifth year, followed by a still further increase the sixth year. After the large losses of the sixth year, consistent decreases in outgo were observed for all treatment during the seventh year, and a still further decrease during the eighth and final year.

It will be noted that each addition has very materially increased the outgo of sulfates over the several meager annual losses—a maximum of 9 pounds from the no-treatment deep tank. Each treatment has been responsible, therefore, for either an enhanced movement of sulfates from the soil and through the subsoil, or a change in the retentive properties of the subsoil, unless it be that calcic and magnesic salts have caused an increased formation of sulfates within the subsoil—a less probable alternative for these particular conditions. It may be assumed with reason that the processes of sulfofication were essentially the same in the treated surface soil, whether underlaid by a sand filter bed or by subsoil. If this be true, it is apparent that even though permitting the passage of part of the sulfates which came from the surface soil, the subsoil depth of one foot has arrested an average

of 445.4 pounds of SO_3 during the initial year. This tendency to stop the downward movement of sulfates diminished in time in the case of additions but not in the control. The more soluble additions were responsible for larger amounts of the alkali-earth bases passing down to the subsoil and, coincident with this greater downward movement of bases, there occurred

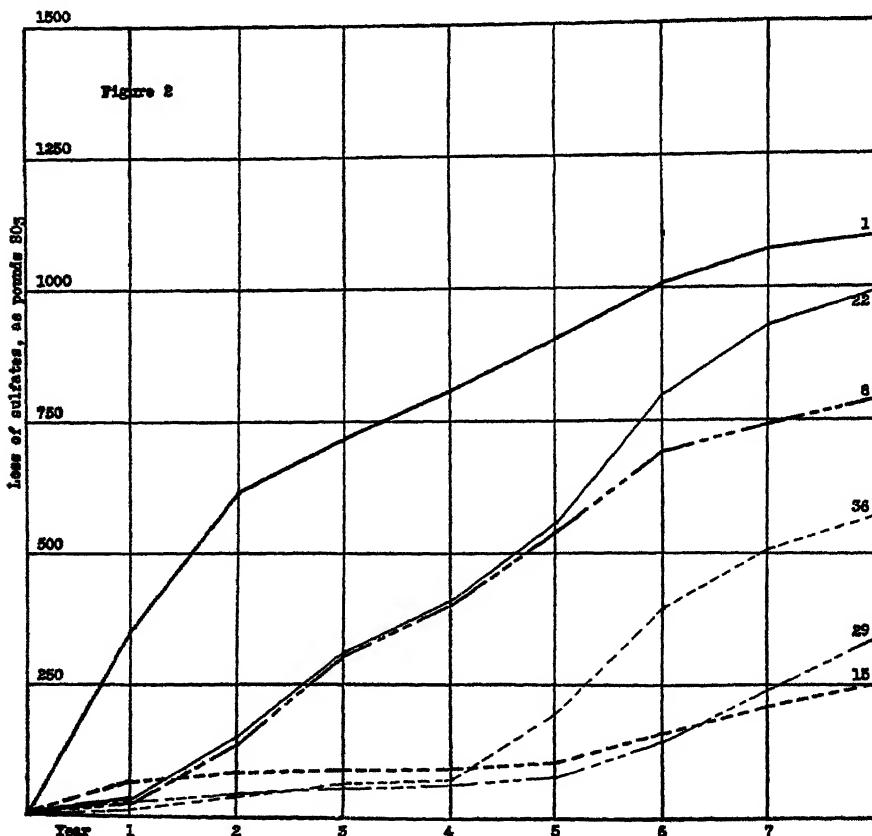


FIG. 2. POUNDS OF SO_3 PER 2,000,000 POUNDS OF SOIL IN LEACHINGS FROM TANKS TREATED WITH CaO AS FOLLOWS:

Surface soil	Tank 1—	8 tons	Surface and subsoil	Tank 22—	8 tons
	8—	32 tons		29—	32 tons
	15—	100 tons		36—	100 tons

a diminished tendency toward sulfate retention. Parallel determinations of occurrences of sulfate sulfur, calcium, and magnesium in the leachings demonstrated that the sulfate absorption is a molecular one, for no marked increase of sulfates occurred in the leachings until increases of calcium and magnesium were also found. The consistent gain in the sulfate yields from subsoil tanks which contained the four oxide and precipitated carbonate

treatments brought the 8-year average proportion for the calcium additions up to more than 91 per cent of the surface soil outgo and that of the magnesium additions to 99.5 per cent. In the case of the three less soluble natural carbonates, however, the lag in the total sulfate outgo from the deep tanks was still very marked, though the amounts leached through the subsoil tanks during the last four years were greater than those from the corresponding surface soil tanks in every instance save one. Hence, after 8 years of leaching, only about 68 per cent of the surface-soil sulfate yield had been found in the subsoil tank leachings, as the average from the limestone, dolomite, and magnesite treatments.

It is therefore established that all of the seven calcic and magnesic materials were responsible for a very extensive acceleration in movements of sulfates from the surface soil. It is also apparent that marked variations in the solubilities of the several materials and sulfate end-products were responsible for wide differences in the amounts of leached sulfates, where the absorptive properties of the subsoil were brought into play. On the other hand, it will be noted that during six years a total difference of over 500 pounds of sulfate outgo obtains between the leaching of 534 pounds from the surface soil and that of 24 pounds from the soil-subsoil. It is evident, therefore, that a marked retentive property is inherent in the subsoil, which has not been subjected to the ameliorating influence of additions of either of the alkali-earth elements. Though the amounts of sulfates leached from the surface soil control and that from the subsoil control are decidedly less than the amounts obtained from any one of the corresponding treated tanks, it is most probably true that the outgo from each control is abnormal because of enhanced sulfification as a result of the thorough aeration incident to digging, screening, and mixing of the moist soil at the beginning of the experiment. Were such extensive sulfate generations and leachings to occur, with no replacements through additions and atmospheric precipitations, the loss of the native stores of sulfur in the surface soil would soon become a fertility factor.

Comparison with Cornell experiments. The results from the 8-ton series especially may be considered in connection with the results obtained from 3000 pounds of CaO by Lyon and Bizzell (2, p. 73). From leachings during a 5-year period from a 4-foot depth of Dunkirk soil, rather high in its CaO content, particularly in the lower zones, these investigators found evidence that lime caused enhancement in sulfification. It is difficult, however, to determine from which zone or zones the sulfates were derived in the experiments of Lyon and Bizzell, where only the 4-foot depth was used. The sulfate totals and disparity between control and treatment were but fractions of those found by us in our lightest treatment. In a later report (3, p. 73) parallel data are given for a Volusia soil of decidedly less CaO content in each of four 1-foot zones. In this case no evidence was given to show increase of sulfate formation from the addition of lime although increased nitrate outgo was shown. They concluded: "Liming the Dunkirk soil did not re-

sult in an increased formation of nitrates, but apparently favored sulfocification. Application of lime to the Volusia soil was accompanied by increased nitri-fication, but had no effect upon the production of sulfates. This would indi-

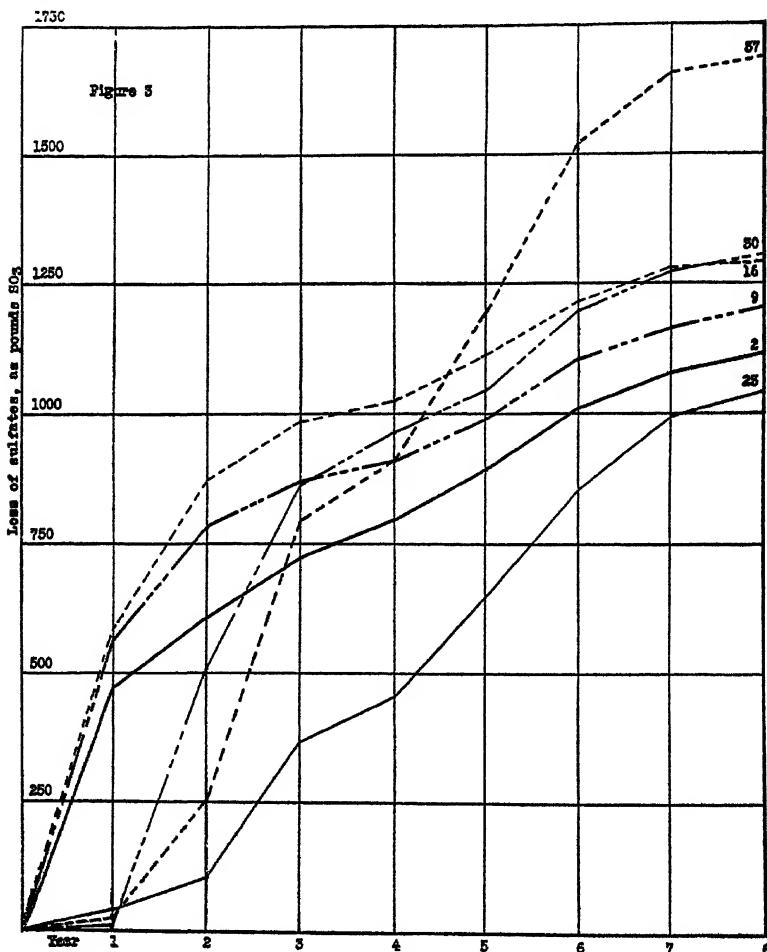


FIG. 3. POUNDS OF SO_3 PER 2,000,000 POUNDS OF SOIL IN LEACHINGS FROM TANKS TREATED WITH MgO EQUIVALENT TO CaO AS FOLLOWS:

Surface soil	Tank 2—8 tons	Tank 23—8 tons
	9—32 tons	30—32 tons
	16—100 tons	37—100 tons

cate that the conditions favorable to one of these fermentations are not always favorable to the other."

Every oxide and carbonate treatment, other than CaO , has largely augmented the 8-year losses of both sulfates and nitrates from the Cumberland

loam used by us. However, every addition of burnt lime ultimately gave large increase in leached nitrates although the heavier additions were initially inhibitory to both nitrification and sulfification. Sulfofication was particularly inhibited in the subsoil with the 32-ton treatment and in the surface soil with the 100-ton treatment. The clay subsoil under the Cumberland loam was able to retain large quantities of sulfates regardless of variation in, or absence of treatment. With 8-ton treatments, this tendency was still marked after the first four years, and even after eight years it was evidenced for all treatments except MgO, being particularly noticeable in the case of the three native carbonates. Heavier additions of the more soluble forms, other than CaO, caused augmented occurrences of the alkali-earth elements and sulfates in the subsoil leachings, even before the end of the first four years. However, disparity between shallow- and deep-tank sulfate losses was still maintained by the heavier additions of the natural carbonates after eight years. The subsoil of the control, when unaltered by influx of added alkali-earth bases continued to manifest a decided ability to restrict the occurrence of sulfates in the leachings. This is amply demonstrated by the fact that the shallow control lost 534 pounds of SO₃ against only 24 pounds from the deep control over a six-year period. These losses represent 69 per cent of the rainfall sulfates in the former case and only 3.1 per cent in the latter. From similar unpublished findings upon a soil treated with soluble sulfate we have found that the leachability of added sulfate and engendered nitrates may be affected differently by treatment. Since this one-foot depth of clay, both subject to and devoid of influx of ameliorating bases added to the overlying soil, has continued to function as a barrier to the passage of sulfates over 8-year and 6-year periods, respectively, the effect and duration of such effect in the 3-foot depth of subsoil of the 5-year Cornell experiments appears problematical. Since our results show that the presence of calcium salts in the subsoil, as a result of leachings from the surface, exerts a marked effect upon the sulfate-retaining properties of the subsoil, it would appear that paucity or abundance of native calcium compounds would influence the action of the lower depths in changing the concentration of sulfates in the surface soil's leachings. Such changes in concentration of leachings have been exerted by the subsoil under the Cumberland loam in both directions, as determined by the treatment applied to the surface soil. Since the Dunkirk and Volusia subsoils vary decidedly in their calcium and carbonate content, it would seem plausible to assume that they would be at variance in their tendencies to alter the sulfate concentrations of the leachings from the surface soil. The points brought out serve to emphasize the value of parallel experimentation with shallow and deep tanks.

THIRTY-TWO-TON TREATMENT

Surface-soil tanks

With the exception of CaO, all of the 32-ton additions caused very decided increases in the leaching of sulfates during the initial year. Calcium oxide depressed the outgo very much below that of the control. The magnesium oxide and carbonate were responsible for the largest losses of sulfates. Next

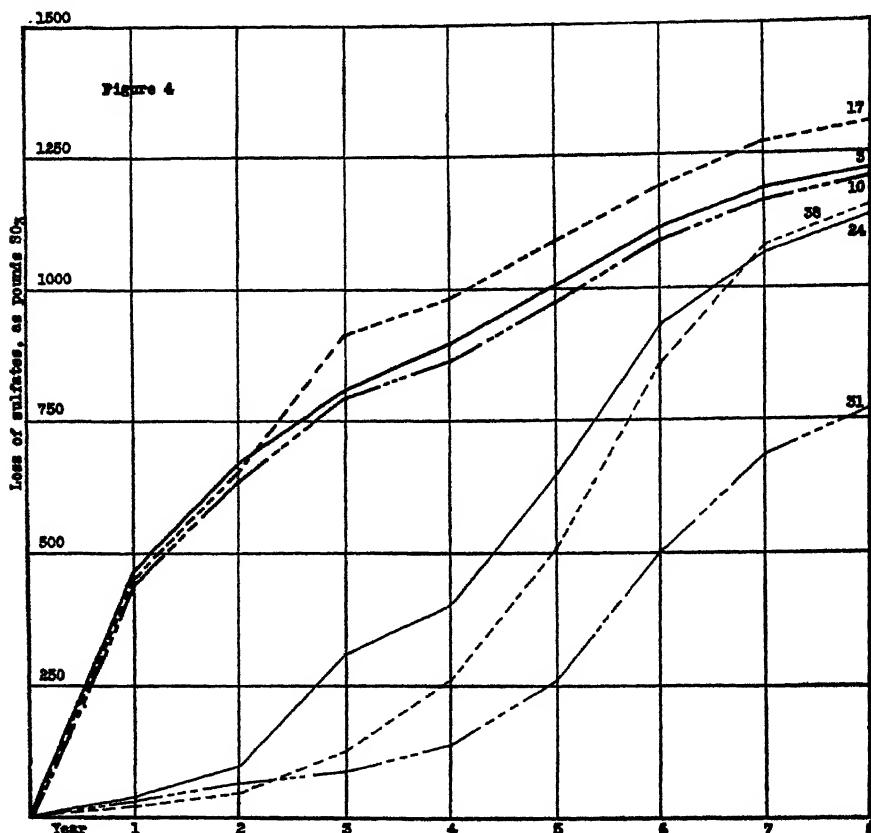


FIG. 4. POUNDS OF SO₃ PER 2,000,000 POUNDS OF SOIL IN LEACHINGS FROM TANKS TREATED WITH CaCO₃ EQUIVALENT TO CaO AS FOLLOWS:

Surface soil	Tank 3—8 tons	Surface and subsoil	Tank 24—8 tons
	10—32 tons		31—32 tons
	17—100 tons		38—100 tons

in order came the precipitated calcium carbonate while the three native carbonates were rather closely grouped in their influence.

During the second year the three native carbonates still exerted an activating influence approaching that of the other forms, exclusive of the burnt

TABLE 4
Sulfate content of leachings from loam soil with treatments equivalent to 32 tons CaO per acre

TANK NUMBER	TREATMENT	AS TO SUBSTR.	TOTAL VOLUME OF LEACHINGS	SO ₄ LEACHED PER 2,000,000 POUNDS OF SOIL									
				1st year		2d year		3rd year		4th year		First 4-year period	
				lbs.	liters	lbs.	liters	lbs.	liters	lbs.	liters	Annual average	Total
8	CaO.....	None	929	19	116	178	86	100	399	146	141	53	39
29	CaO.....	Clay	944	25	22	4	12	16	63	12	75	94	49
9	MgO.....	None	932	567	216	89	39	228	911	81	116	62	35
30	MgO.....	Clay	968	18	489	361	97	241	965	78	152	83	32
10	CaCO ₃	None	1008	448	187	155	73	216	863	113	111	76	40
31	CaCO ₃	Clay	1024	29	30	24	50	33	133	128	240	185	84
11	MgCO ₃	None	915	551	203	119	61	234	934	119	103	44	34
32	MgCO ₃	Clay	1034	55	594	430	138	304	1217	117	164	73	29
12	Limestone.....	None	1082	399	172	123	65	190	759	114	112	73	42
33	Limestone.....	Clay	1013	31	28	74	62	49	195	142	261	175	78
13	Dolomite.....	None	1026	403	238	197	80	230	918	158	153	125	74
34	Dolomite.....	Clay	1038	39	78	225	98	110	440	178	278	188	98
14	Magnesite.....	None	1077	426	176	118	82	201	802	116	107	111	35
35	Magnesite.....	Clay	1086	21	45	269	138	118	473	227	300	150	66
43	Wollastonite.....	Clay	1127	35	26	64	46	43	171	115	235	169	91
44	Serpentine.....	Clay	1207	42	19	7	14	21	82	6	38	33	26
<i>Indices of rainfall.....</i>			47.78	56.54	63.32	47.79	51.41	54.21	50.37	55.63	...

lime. During the third and fourth years, the yields were progressively and consistently decreasing. However, a reversion toward increase of sulfate outgo followed during the fifth and sixth years, after which came progressive depressions in the seventh and eighth years. In every case, both total and average annual results in the first half were larger than the corresponding amounts for the second half of the 8-year period. The totals for the 8 years were very nearly equivalent for the MgO, CaCO₃, MgCO₃, and magnesite, the limestone results coming next in order. The smallest outgo of sulfates for the full period came from the burnt lime, while the greatest came from the dolomite.

Soil-subsoil tanks

The amount of sulfates which passed from every treatment and through the subsoil was relatively meager during the first year and but a fraction of the amount which passed from the surface soil of corresponding treatment. Each treatment, however, caused a loss in excess of that from the deep control. It will be noted that there were no consistent increases during the second year from the treatments of CaCO₃, limestone, dolomite, and magnesite. However, a very striking increase was obtained from both MgO and MgCO₃. The limestone and CaCO₃ were still rather inactive during the third year, but both dolomite and magnesite had effected a material increase in the passage of sulfates. With the exception of precipitated CaCO₃, which still had failed to show any progressive increase in sulfate outgo, all treatments showed a smaller sulfate yield for the fourth year than for the third year. There was a general tendency toward progressive increases in outgo during the fifth and sixth years, followed by a progressive decrease through the seventh and eighth years. The average annual and the total losses from the deep tanks for the first 4-year period were greater than the corresponding figures from the shallow tanks in the case of the MgO and MgCO₃ treatments, while the reverse was true in the case of precipitated CaCO₃, limestone, dolomite and magnesite.

The results from tank 29, CaO treatment, are in decided contrast to those from the other tanks. The average annual outgo from this oxide was only 16 pounds for the first 4-year period, while that for the full 8-year period was only 37 pounds. The sulfate leachings from the corresponding surface-soil tank, No. 8, were also decidedly lower than those from the other treatments for both 4-year periods. The persistence of calcium hydrate in the soil of those tanks was established by a study of the speed of the reversion of the CaO to CaCO₃ which has been reported (6). The occurrence of Ca(OH)₂ in each leaching has been determined. The average hydroxide concentration for the several annual leachings are given in table 6. Those of the surface soil leachings were appreciable during the first three years, especially for the initial year. Though a decided drop occurred during the fourth year, the hydroxide persisted in the leachings through the fifth year. The persistence

of the calcium hydrate has been responsible for a marked depression in sulfate outgo for all years as compared with every other oxide or carbonate treatment and for the first year more especially in a comparison against the shallow con-

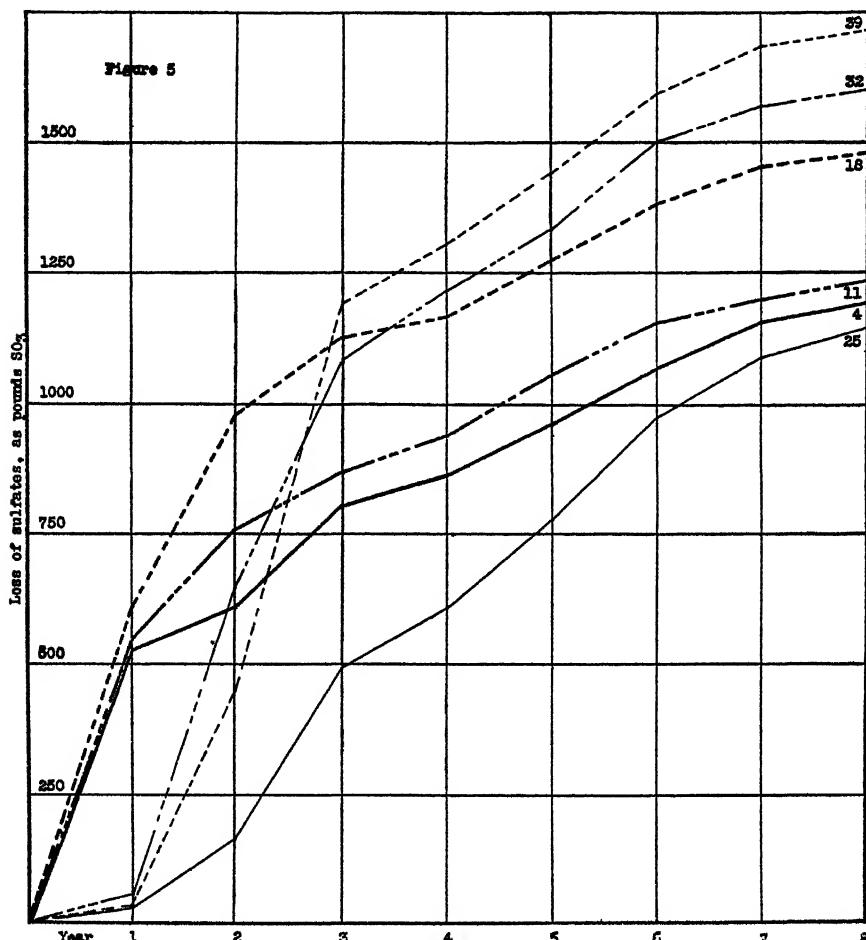


FIG. 5. POUNDS OF SO₄ PER 2,000,000 POUNDS OF SOIL IN LEACHINGS FROM TANKS TREATED WITH MgCO₃ EQUIVALENT TO CaO AS FOLLOWS:

Surface soil	Tank 4—8 tons	Tank 25—8 tons
	11—32 tons	32—32 tons
	18—100 tons	39—100 tons

trol. Though not all-conclusive, this indicated depressed generation of sulfates in the surface soil. But, in spite of the ready solubility of Ca(OH)₂, the subsoil stopped its downward movement, and also that of the sulfates, which surface soil leachings indicated had passed into the subsoil.

Both wollastonite and serpentine increased the outgo of sulfates. However, after the initial year, a consistently larger yield came from the calcium silicate. The total of 171 pounds from this material during the first 4-year period was twice as large as the amount which passed from the serpentine tank. The disparities during each of the last four years were still more marked, so that after eight years a total of 781 pounds of SO₃ had passed from the wollastonite treatment, as against only 185 pounds from the serpentine addition. As previously pointed out by the senior author (5, p. 19), the wollastonite used was very much more readily hydrolyzed than was the serpentine. Consequently the wollastonite addition has resulted in a continuous treatment of calcium bicarbonate, which has been more efficacious than have the meager amounts of magnesium bicarbonate derived from the very insoluble silicate of magnesium in forcing the downward movement of sulfates.

ONE-HUNDRED-TON TREATMENT

Surface-soil tanks

The 100-ton CaO treatments have shown the same depressing influence as the 32-ton additions.

All other treatments show the greatest quantities of sulfates passing out during the initial year, with successive decreases through the second, third and fourth years. An upward trend is exhibited by all treatments, save CaO, for the fifth and sixth years, followed by successive decreases during the seventh and eighth years. The average annual and the total outgo of sulfates during the first 4-year period were both greater than the analogous amounts for the second 4-year period for all treatments, except CaO. In this series the sulfates leached from the dolomite during the 8-year period amounted to more than the outgo from the magnesium carbonate. This fact will be considered in dealing with the origin of the sulfur lost from the soil through leaching. As will be seen, however, by reference to table 1, the dolomite treatment carries an appreciable amount of SO₃ in the form of sphalerite (zinc sulfide) and the heavy addition means that large quantities and extensive surfaces of the sulfide are subjected to chemical and bacterial oxidative reactions.

Subsoil tanks

In the CaO tank of this series the average annual outgo of 16 pounds for the first 4-year period increased to an annual average of 127 pounds for the last four years. But the corresponding annual averages for the surface soil alone were only 22 pounds and 42 pounds. The 8-year total exceeded that of the shallow tank by 317 pounds. It may be that the leached lime either directly caused an increased formation of sulfates in the subsoil or a release by the subsoil of such sulfates as it may have held prior to the influx of calcium hydroxide and other calcium combinations. The MgO and MgCO₃ treat-

TABLE 5
Sulfate content of leachings from loam soil with treatments equivalent to 100 tons CaO per acre

TANK NUMBER	TREATMENT	AS TO SUBSOIL	TOTAL VOLUMES OF LEACHINGS	SO ₃ LEACHED PER 2,000,000 POUNDS OF SOIL.								
				First 4-year period				Second 4-year period				
				1st year	2d year	3rd year	4th year	5th year	6th year	7th year	8th year	
			liters	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	
15	CaO.....	None	806	67	15	4	1	22	87	16	60	54
36	CaO.....	Clay	965	17	30	15	3	16	65	130	199	114
16	MgO.....	None	825	581	291	114	41	257	1027	88	102	61
37	MgO.....	Clay	983	25	229	545	113	228	912	278	334	130
17	CaCO ₃	None	914	460	287	168	63	245	978	110	102	82
38	CaCO ₃	Clay	968	27	12	78	138	64	255	247	353	224
18	MgCO ₃	None	830	618	364	143	42	292	1167	109	110	64
39	MgCO ₃	Clay	928	38	410	742	113	326	1303	138	154	87
19	Limestone.....	None	972	402	215	139	64	205	820	119	106	70
40	Limestone.....	Clay	1069	40	87	60	48	59	235	150	316	227
20	Dolomite.....	None	906	417	325	279	130	288	1151	286	300	237
41	Dolomite.....	Clay	1006	27	18	89	34	42	168	315	560	385
21	Magnesite.....	None	987	509	181	160	70	230	920	116	128	88
42	Magnesite.....	Clay	1054	22	22	138	95	69	277	226	399	246
<i>Inches of rainfall.....</i>				47.78	56.54	63.32	47.79	51.41	54.21	50.37
												55.63

ments both increased the sulfate outgo during the second year with still further increases during the third year after which there was a drop. For the first 4-year period almost as much sulfate was lost through the subsoil as from the surface soil, while for the $MgCO_3$ additions the outgo was actually greater. The precipitated $CaCO_3$ and natural carbonates, however, caused a decidedly smaller loss of total sulfates from soil plus subsoil than from the surface soil alone. The amount of SO_3 lost from every subsoil tank during the second 4-year period was decidedly larger than that of the corresponding shallow tank. The fifth and sixth years' losses from the MgO and $MgCO_3$ tanks were greater than those of the fourth year. This increase was followed by a progressive decrease during the seventh and eighth years. The 8-year losses from those two materials were also greater when the leachings passed through the subsoil. The excess losses of 380 and 231 pounds of SO_3 from subsoil tanks treated with MgO and $MgCO_3$ demonstrate that the leached sulfates were derived in part from the subsoil. This does not obtain, however, in the case of the three natural carbonates and in the case of precipitated $CaCO_3$.

EFFECT OF FORM AND RATE OF TREATMENT ON LOSS OF SULFATES

The effect of rate of treatment is shown in the graphs, figures 1 to 8.

Burnt lime

Previously reported (6) residual carbonate analyses showed that the hydrate of the 8-ton CaO application had practically all passed from that form after a few weeks. But the direct CaO absorption and carbonation reactions continued for a much longer period where the hydrate persisted from the two excessive rates of 32 and 100 tons. This difference in the persistence of calcium hydrate is reflected in the larger sulfate outgo of the 8-ton treatment and the smaller loss from each of two heavier treatments, especially in the case of the surface soil for the first three years. The lesser handicap imposed upon the soil treated at the 8-ton rate during the period required for reversion of $Ca(OH)_2$ to $CaCO_3$ was, however, apparently overcome and followed by accelerated sulfofication. As a result totals for both the initial 4-year period and the full 8-year period approached the corresponding totals from calcium carbonate for both depths. Yet, the persistence of the $Ca(OH)_2$ in the two heavier treatments continued to depress the outgo so that the total for the 8-year period in the 32-ton treatment amounted to only 778 pounds, or an annual average of 97 pounds, while a still smaller total of 256 pounds, or an annual average of 32 pounds, came from the 100-ton treatment. If decreased outgo and depressed sulfate generation be identical, it would appear that the excessive amounts of lime partially inhibited sulfofication. As an alternative, however, it might be assumed that the burnt lime had not depressed sulfofication and that such had continued normally, or even with acceleration, in the more open and better aerated soils containing the heavier

treatments in particular. It would follow, then, that such engendered sulfates were less soluble in the $\text{Ca}(\text{OH})_2$ -impregnated water, and hence were not washed out in the leachings. This alternative finds support from two angles. First, the rainfall which passed through heavy CaO additions often contained less sulfates as leachings than it did as rain water. Secondly, the

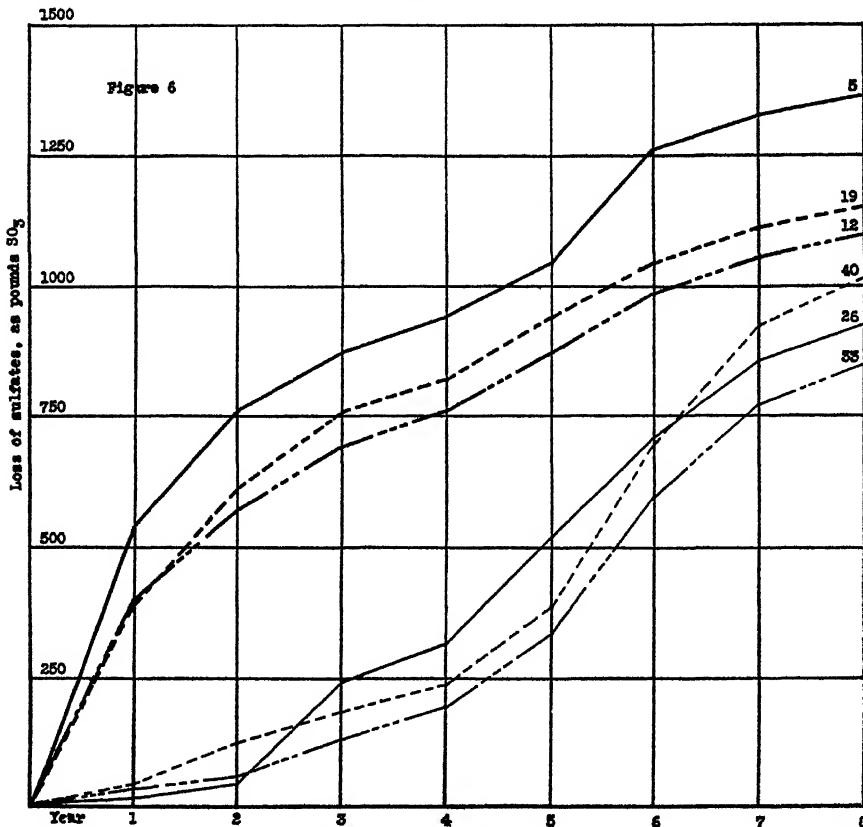


FIG. 6. POUNDS OF SO_4 PER 2,000,000 POUNDS OF SOIL IN LEACHINGS FROM TANKS TREATED WITH LIMESTONE EQUIVALENT TO CaO AS FOLLOWS:

Surface soil	Tank 5—8 tons	Surface and subsoil	Tank 26—8 tons
	12—32 tons		33—32 tons
	19—100 tons		40—100 tons

initial inhibition of the parallel biochemical process of nitrification was followed by intensive acceleration after the first annual period.

Solubility of calcium sulfate in lime water

In searching for data upon the solubility of CaSO_4 in solutions of $\text{Ca}(\text{OH})_2$, we have found only the data of Cameron and Bell (1), given also by Seidell

TABLE 6
Average normality of Ca(OH)_2 in each annual leaching from tanks treated with CaO at the rate of 8, 32 and 100 tons as determined from the analysis of each periodic leaching

(10). These investigators subjected aqueous and lime water suspensions of gypsum to constant agitation at 25°C. for two weeks and determined the concentration of CaSO_4 . They used eleven aqueous solutions of $\text{Ca}(\text{OH})_2$ containing 0.062–1.166 gm. CaO per liter. With increase in concentration of $\text{Ca}(\text{OH})_2$ there occurred a decrease in amount of CaSO_4 in solution. However, the minimum concentration of CaSO_4 given by Cameron and Bell was much greater than that of the maximum concentration found in the tank leachings. Calculating SO_3 losses to equivalence of CaSO_4 , the maximum concentration possible in our leachings was 0.1884 gm. per liter. But this concentration is the CaSO_4 equivalent of the 0.3231-gm. BaSO_4 determination upon the composite which gave the maximum annual loss of 742 pounds of SO_3 from the 100-ton MgCO_3 treatment. Furthermore, the cited data were obtained from gypsum, rather than from freshly precipitated $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, such as would be found in the soil. We have, therefore, sought additional data, particularly with reference to the freshly precipitated hydrated material.

Before considering such data, however, it would be well to consider the concentrations of $\text{Ca}(\text{OH})_2$ in the drainage waters of the six tanks which received applications of CaO. These concentrations for each annual period were derived by averaging the hydroxide titration values of the several periodic leachings and are given in table 6. No $\text{Ca}(\text{OH})_2$ passed from the 8-ton additions made to either shallow or deep tanks. The presence of hydroxide was established for each of the first five years in the case of the surface soil leachings from the 32-ton additions, the maximum occurring during the first annual period, with a decided drop for the second and third years and with still further decreases, progressively for the fourth and fifth years. No $\text{Ca}(\text{OH})_2$ ever appeared in the leachings which passed through the subsoil in the tank receiving CaO at this rate. The initial concentration and that maintained through the first three years were very much higher for the surface-soil leachings from the 100-ton additions than for the 32-ton treatment. Some $\text{Ca}(\text{OH})_2$, derived in the main from the 100-ton treatment residues in the lower zones of surface soil, has persisted intermittently throughout the 8-year period. Again, however, as in the 32-ton additions, no calcium hydroxide has passed through the 1-foot zone of clay subsoil.

With these figures before us, we may better consider the solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ as given in table 7 and apply such data as explanatory of the sulfate losses induced by CaO additions as given in tables 3, 4 and 5. Analysis A reported in table 7 was made in 1920 upon an aged concentrate standing over a large quantity of solid-phase $\text{Ca}(\text{OH})_2$. Analysis B was made in 1923 upon the same solution again brought to saturation after the addition of water. The normality values found in both analyses for saturation at 25°C. were higher than those given by Seidell (10). The initial and final titration values of the $\text{Ca}(\text{OH})_2$ solutions, varying only within analytical error, show that no $\text{Ca}(\text{OH})_2$ was changed from the solution phase to the solid

phase by contact with the excess of solid-phase calcium sulfate. The table shows that the highest $\text{Ca}(\text{OH})_2$ concentrations in the 100-ion-treatment leachings, 0.02113 normal, somewhat less than one-half saturation, could carry at least 1.75 gm. of calcium sulfate per liter. This amount is more than 9 times that of the heaviest CaSO_4 content found in the annual leachings. Contact of engendered sulfates and soil water impregnated with $\text{Ca}(\text{OH})_2$ could hardly be such as to insure saturation of the solid in the solvent. The ratio of more than 9 to 1 would serve, however, as an offset to the lesser opportunity of the soil water to effect concentration of sulfates, were such widely diffused throughout the soil. We have other unpublished data relative to the influence of lime upon the outgo of applied sulfates from another soil. These data establish the tendency of the lime-treated soil to retard

TABLE 7

The solubility of anhydrous and freshly precipitated calcium sulfate in solutions of calcium hydroxide at 25°C.

ANALYSIS A, 1920— AGITATION INTERMIT- TENTLY FOR 3 HOURS AND 16 HOURS CONTACT— 5.0 GM. CHARGES PER 500 CC. OF WATER		ANALYSIS B, 1923—72 HOURS CONTACT WITH FREQUENT AGITATION— 20 GM. CHARGES PER 500 CC. OF WATER						
		Anhydrous calcium sulfate*			Freshly precipitated $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$			CaSO_4 dissolved per liter of $\text{Ca}(\text{OH})_2$
Anhydrous calcium sulfate*	Normality of $\text{Ca}(\text{OH})_2$	Before con- tact with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	After contact with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	CaSO_4 dissolved per liter of $\text{Ca}(\text{OH})_2$	Normality of $\text{Ca}(\text{OH})_2$	Before con- tact with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	After contact with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	
Normality of $\text{Ca}(\text{OH})_2$	CaSO_4 dissolved per liter of $\text{Ca}(\text{OH})_2$	gm.	gm.	gm.	Normality of $\text{Ca}(\text{OH})_2$	Before con- tact with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	After contact with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	gm.
0	1.9160	0	0	2.1695	0	0	0	2.0464
0.0047	1.8600	0.00440	0.00430	1.8633	0.00448	0.00440	0.00440	1.9630
0.0119	1.7740	0.01120	0.01090	1.9240	0.01121	0.01101	0.01101	1.8996
0.0238	1.6560	0.02240	0.02190	1.7980	0.02240	0.02201	0.02201	1.7694
0.0475	1.5620	0.04480	0.04480	1.7303	0.04480	0.04480	0.04480	1.7607

* From J. W. Owen & Co., Philadelphia.

the outgo of added sulfates during the persistence of $\text{Ca}(\text{OH})_2$. If sulfates had accumulated in excessive amounts during the persistence of $\text{Ca}(\text{OH})_2$ in the Cumberland loam, it would be expected that the rapid removal of sulfates would follow the disappearance of the hydroxide. But instead of such a marked transition in rate of sulfate outgo, there has occurred a gradual increase in sulfate emissions, as though the soil flora were slowly regaining their vigor and ability to manufacture sulfates, after the continued excessive causticity and during the maintenance of a materially lessened, though still positive, alkalinity.

These data, as a whole, do not prove that the relative decrease in sulfate outgo caused by the heavier treatments was due entirely to initial biological inhibition, nor do they establish the fact that the heavy treatments main-

tained such an inhibition. But they do establish the fact that there was in the early stages an inhibitory influence of some kind. The initial inhibition disappeared in time as a result of the carbonation of the excess of $\text{Ca}(\text{OH})_2$. This chemical transition was the dominant causative factor controlling initial inhibition and later acceleration, whether the effect be considered the result of biochemical, physical or chemical changes in the soil, or a combination of the three.

Magnesium oxide

The effect of MgO , however, was different from that of CaO . As indicated by the composition of the leachings, the quantity of MgCO_3 formed from the oxide of magnesium was such as to constitute a treatment of MgCO_3 . This carbonate, both applied and oxide-derived, was more rapidly and intensively fixed by the soil and at the same time the unabsorbed excess was more quickly and intensively leached. Furthermore, any hydrated MgO derived from the MgO additions was very much less soluble than the hydrate of calcium. Consequently, there was no problem as to repressed solubility of soil-engendered magnesium sulfate. The heavy sulfate leachings from the MgO additions indicated that the low concentration of $\text{Mg}(\text{OH})_2$ in the soil water did not inhibit nor depress sulfification. It will be noted that the sulfate losses of the initial year, those of the first 4-year period, and those of the full 8-year period increased in the order of increasing rates of treatment. Thus, the surface soil tanks treated at the rates of 8, 32 and 100 tons lost 1118, 1205, and 1297 pounds, respectively.

In the case of the subsoil tanks the peak of the sulfate outgo came during the third year for both 8-ton and 100-ton MgO additions. But in the case of the 32-ton treatment the greatest losses occurred during the second year. This finding evidently involves some system balance, for the presence of magnesium bicarbonate in the leachings was observed to have occurred in the same manner. Furthermore, the MgCO_3 additions behaved in the same way, with reference both to sulfates and bicarbonate of magnesium. That is, the subsoil drainages from the magnesium oxide and carbonate tanks were for a time low in both their sulfate and magnesium bicarbonate contents, and then with the advent of increased concentration of one substance there occurred a parallel increase in that of the other.

Calcium carbonate

During the third year which was one of abnormal rainfall the 8-ton deep tank lost three times the amount lost during the first two years. A drop during the fourth year was followed by increases during the fifth and sixth years, after which occurred progressive decreases during the seventh and eighth years. But in the case of the 32-ton addition in the deep tank, the small amounts of the first four years were succeeded by increased losses during the fifth, sixth, and seventh years, with a decrease in the eighth year. Where

the CaCO_3 additions to the deep tank were at the 100-ton rate, the small losses of the first three years were followed by maintained increases during the fourth, and more particularly the fifth, sixth and seventh years, after which occurred a decided drop. Accordingly, the 8-year total SO_3 losses from the 32-ton treatment amounted to but 770 pounds, as contrasted with corresponding totals of 1133 pounds and 1150 pounds for the 8-ton and 100-ton treatments, respectively. Likewise, the first 4-year period total from the 32-ton addition was less than that of either the 8- or 100-ton addition. It would seem that the 32-ton treatment would be sufficiently extensive to give a thoroughly disseminated treatment throughout the mass of soil, so that the soil-water would become saturated with calcium bicarbonate. Both 32- and 100-ton additions should afford directly dissolved calcium in amounts greater than the amount dissolved from the 8-ton treatment. Thus, if calcium carbonate, or bicarbonate were to be considered as depressive, both 32- and 100-ton treatments would be expected to yield smaller quantities of sulfates than those coming from the 8-ton treatment. But during each 4-year period the sulfate outgo from the 32-ton treatment lagged behind the losses from both the 8- and 100-ton additions. As the converse of the magnesium additions, where both magnesium bicarbonates and sulfates appeared first and for a time most extensively in the leachings from the 32-ton addition of magnesium oxide and carbonate, unpublished data from these tanks show that the 8- and 100-ton CaCO_3 treatments both yielded more CaCO_3 than did the 32-ton treatment during the first and second 4-year periods, and of course, greater also for the full 8-year period. As in the case of the MgCO_3 converse, at the same equivalent rate, a system balance would also seem to be of effect in the 32-ton CaCO_3 treatment.

Magnesium carbonate

The total amount of sulfates from the magnesium carbonate additions have increased slightly with each increase of treatment. The 8-, 32- and 100-ton treatments have caused leaching totals of 1189, 1234, and 1482 pounds, respectively, from the surface soil. In each case, the maximum outgo has occurred during the initial year, with the next largest outgo during the second year and the third largest during the third year. After the third year the amounts passing from the residual sulfur reserves are comparatively small. In this connection it should be pointed out that a number of the annual sulfate leachings from this treatment are actually less than the amounts found to have been brought down by rain water. This observation is common to a number of the other treatments. It is rather interesting to note that, particularly in the case of the subsoil tanks, a treatment may so retard the passage of sulfates as to cause the sulfate concentration of the leachings to be lower than that of rainfall, before the treatment begins to push itself and the sulfate of its basic ion through the subsoil, and that the same partial accumulation of the rainfall sulfates may be evidenced after the maxima sulfate yields have passed.

Limestone-dolomite-magnesite

The three native carbonates acted in a similar manner at each rate, by inducing the largest losses of sulfates from the surface soil during the initial year with consistent, progressive decreases during the following three years. Each of the three natural products also caused an upward trend in the outgo curve, with practically identical amounts during the fifth and sixth years, followed by a downward trend during the seventh and eighth years. The first 4-year-period yield and the total outgo from the limestone, dolomite, and magnesite were rather close for the 8-ton additions. The sulfate outgo, however, from the 32- and 100-ton additions drew away from the losses shown by the 8-ton treatment during the first 4 years with a still further disparity during the second half of the 8-year period. It would appear that the sulfide impurity of the dolomite had served as a source for increased sulfate generation particularly after the fourth year.

Where the three natural materials were applied to the deep tanks at the 8-ton rate, the totals for the first 4-year period were less in each case than the respective initial year losses from the surface soil alone. The largest subsoil outgo of the first 4-year period came during the third year in each case. During the fifth year there was a marked increase in the sulfate outgo from each material, the largest outgo for the second period coming, however, in the sixth year, after which there was a progressive downward tendency for the last two years.

In the case of the 32-ton applications, the largest annual loss of the first 4-year period also occurred in the third year. During the fifth, sixth and seventh years, all three materials gave decided increases over corresponding losses of the fourth year, followed by a very decided decrease for each addition during the eighth annual period.

There were no greatly accelerated movements of sulfates through the subsoil from either of the three natural products at the 100-ton rate for any one of the first four years, with the possible exception of magnesite during the third year. During the first three years of the second 4-year period, however, the amounts of sulfates leached through the subsoil were materially augmented particularly in the case of the dolomite, the yield from which was in excess of that from any one of the shallow tanks. This indicates either the passage of the sphalerite-derived sulfates from the dolomite treatment in the surface soil or else an activated sulfate generation or sulfate liberation in the subsoil as induced by the specific ratio of calcium-magnesium salts supplied by the dolomitic limestone.

RELATION OF TOTAL SULFATE LOSSES TO SOURCES OF SULFUR

The shallow tanks have three sources from which the leached sulfates may have been drawn—soil, treatment, and rainfall. The deep tanks have the subsoil as an additional source. Although the SO₃ content of the subsoil

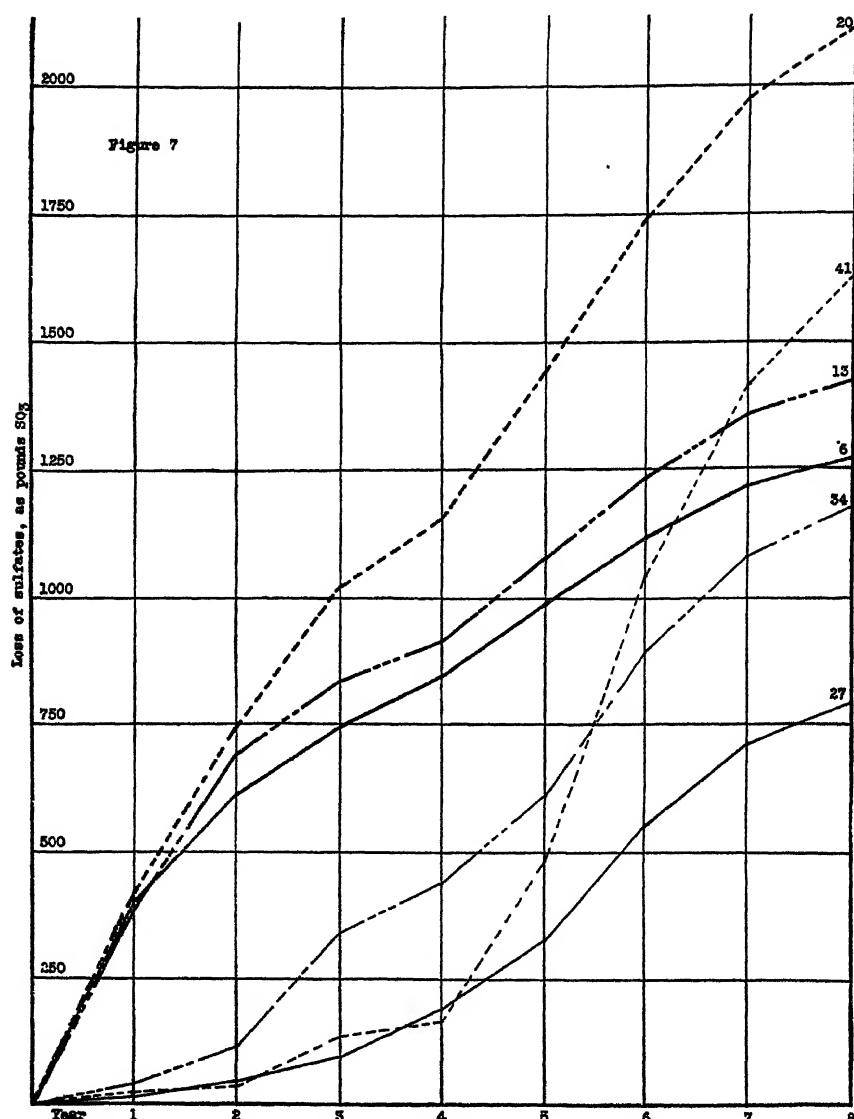


FIG. 7. POUNDS OF SO_3 PER 2,000,000 POUNDS OF SOIL IN LEACHINGS FROM TANKS TREATED WITH DOLOMITE EQUIVALENT TO CaO AS FOLLOWS:

Surface soil	Tank 6—	8 tons	Surface and subsoil	Tank 27—	8 tons
	13—	32 tons		34—	32 tons
	20—	100 tons		41—	100 tons

was found to be less than that of the surface soil, there was more SO_3 supplied by the clay than by the soil, because of the 1-foot depth of the subsoil, as against 8 inches of surface soil. In considering the relationship of outgo to the amounts of sulfur added in treatments, we have to deal only with MgO , MgCO_3 , CaCO_3 , dolomite, and magnesite, since the limestone and burnt lime were sulfur-free.

It is of course difficult, if not impossible, to determine definitely the source of the sulfates found in the leachings; yet, certain proportionate relationships may be established. For instance, in some cases the annual sulfate outgo was less, and in others decidedly more, than the amount of SO_3 washed down by the rainfall. In other instances the amounts of sulfates in the leachings which passed through the subsoil were greater than the amounts leached from the surface soil alone, demonstrating the fact that a fraction of the outgo was necessarily derived from the subsoil. Such relationships for the 8-year period are given in table 8.

Eight-ton treatment

Since each treated shallow tank gave a sulfate outgo greater than that of the rainfall, it must be assumed that some of the leached sulfates were derived from either treatment or soil, or both. The sulfate total carried from the soil and through the subsoil was greater than that brought down by rainfall in the case of each of the three additions, MgO and precipitated carbonates of calcium and magnesium, but it was less for the burnt lime, limestone, dolomite, and magnesite. However, if all rainfall sulfates were leached through the surface soil, the 7 treatments show an average per acre loss of only 167 pounds of SO_3 to be charged jointly against soil and treatment impurities. Assuming no sulfur additions to the surface soil from treatment or rainfall during the 8-year period, all of the seven treatments at this rate caused losses in excess of one-half of the store present in the soil at the beginning of the experiment. When considered as the proportionate part of the sulfur carried by both soil and subsoil, each sulfate outgo from the deep tank is less than one-fifth of that possible from these two sources. The 6-year-period outgo of sulfur from the shallow control was less than the sulfate content of rainfall and only 25.2 per cent of the amount originally present in the soil. The outgo from the subsoil control was but one-twenty-second of that from the shallow control and only 0.5 per cent of the total native sulfur content of soil and subsoil.

The yield of sulfates in the leachings over the 8-year period was many times the amount added through the impurities of the treatment, for all of those additions, save dolomite, where the proportions were only 1.81 to 1 for the shallow tank and 1.13 to 1 for the deep tank.

When the sulfate losses from the surface soil are expressed as per cent of the total sulfur supplied from all sources, all treatments show a loss of one-third or more of that possible. A maximum of 19.3 per cent and a minimum

TABLE 8
Relation of total SO₃ leached to total available in soil, treatments and rainfall for the whole 8-year period

TREATMENT	SO ₂ CARRIED IN LEACHINGS					
	From surface soil only			From surface soil and subsoil		
	Total amount per 2,000,000 lbs. of soil	As per cent of sulfur content of soil	As multiple of SO ₂ added in treatment	As per cent of total available from all sources	As per cent of total available from rainfall	As per cent of SO ₂ in rainfall
	lbs.	per cent	per cent	per cent	per cent	per cent
<i>8-ton rate</i>						
CaO.....	1104	52.1	37.26X	107.3	35.1	992
MgO.....	1118	52.7	16.97X	108.6	35.2	1150
CaCO ₃	1222	57.6	32.13X	118.7	37.9	1133
MgCO ₃	1189	56.1	115.5	37.3	1146
Limestone.....	1261	59.5	112.8	40.0	931
Dolomite.....	1271	60.0	1.81X	123.4	33.0	793
Magnesite.....	1206	56.9	36.50X	117.2	37.9	815
					16.7	24.70X
<i>32-ton rate</i>						
CaO.....	778	36.7	75.6	24.7	293
MgO.....	1205	56.8	10.04X	117.1	36.9	1310
CaCO ₃	1203	56.7	4.18X	116.8	35.0	770
MgCO ₃	1234	58.2	8.34X	119.9	37.4	1600
Limestone.....	1100	51.9	106.9	34.9	851
Dolomite.....	1428	67.4	0.51X	138.8	24.0	1182
Magnesite.....	1171	55.2	8.87X	113.8	35.7	1216
						24.9

	<i>100-ton rate</i>						
CaO.....	257	12.1	24.9	8.2	573	11.7
MgO.....	1297	61.1	3.46X	126.0	36.8	1687	34.5
CaCO ₃	1308	61.7	1.45X	127.1	32.3	1150	23.5
MgCO ₃	1482	69.9	3.20X	144.0	41.0	1713	35.0
Limestone.....	1151	54.3	111.9	36.6	1019	20.8
Dolomite.....	2093	98.9	0.24X	203.7	17.6	1627	33.3
Magnesite.....	1296	61.1	3.14X	125.9	36.4	1236	25.3
<i>32 tons of material applied</i>							
Wollastonite.....	781	16.0
Serpentine.....	185	3.8
<i>Control—no treatment</i>							
None.....	534*	25.2	69.0	18.5	24*	0.5
					
						3.1	0.4

* Six years.

of 12.0 per cent of that available from all sources, including the subsoil, were found to have passed through the treated soil-subsoil tanks. In the controls, only 18.5 per cent of that possible from the surface-soil control and but 0.4 per cent of that possible from the deep-tank control were found in the total leachings after 6 years.

Thirty-two ton treatment

Either partial sterilization, increase in the soil's retentive properties, depressed solvent action, desulfification, or a combination of these factors resultant from this CaO treatment was responsible for a sulfate outgo of but 36.7 per cent of the amount originally present in the surface soil, and only 6.0 per cent of that contained originally by both soil and subsoil. In each of the other oxide and carbonate treatments in the shallow tanks, the leached SO₃ amounted to more than 55 per cent of that native to the soil. The several magnesic materials caused the deep tanks to lose from one-fourth to one-third of the sulfur originally present in the soil plus subsoil. As previously noted, the smaller outgo from the 32-ton CaCO₃ treatment held not only for sulfates, but also for calcium; i.e., a smaller total of both sulfates and calcium passed through the subsoil from 32-ton equivalent than from either the 8-ton or the 100-ton equivalent. Expressed as per cent of the total sulfates supplied to the surface soil from all sources, the MgO, CaCO₃, MgCO₃, limestone, and magnesite each had induced a sulfate outgo equivalent to slightly more than one-third of that possible; while the CaO and dolomite were responsible for losses of smaller proportions. Based on amounts from all sources, including the subsoil, the deep-tank losses varied from a minimum of 4.9 per cent, in the case of CaO, to a maximum of 26.4 per cent, in the case of MgCO₃.

Both wollastonite and serpentine failed to push through an amount of sulfate equivalent to that of the rainfall. The SO₃ leached from the serpentine tank was only 18 per cent of that which was brought to it by rainfall. The wollastonite and serpentine yielded 13.1 per cent and 3.0 per cent, respectively, as the fractions of sulfur available from all sources.

One-hundred-ton treatment

The sterilizing activities and other factors mentioned in the discussion of the 32-ton results were of still greater effect in the 100-ton addition, which was responsible for losses approximately one-eighth of the total sulfur in the surface soil. Since the amount of sulfates which passed through the deep tank which contained CaO was more than twice as great as the amount which was lost from the corresponding shallow tank, it is evident that the larger fraction of the sulfate outgo was derived from the subsoil. The heavy CaO treatments so depressed the surface-soil sulfate outgo that the amount leached represented only one-fourth of the amount brought down in the rain water. The sulfates derived from the subsoil increased the sulfate yield to 55.7 per cent of the

sulfur brought down in the rain water. The sulfate leachings from the heavy CaO additions were depressed to 8.2 per cent and 9.7 per cent of the amounts derived from all sources, for the surface soil and the soil-subsoil, respectively.

Calculated to 8-year totals, with the exception of CaO, the sulfate outgo from each surface soil tank treated at the 100-ton rate was in excess of the amount carried by the rain water. The same was true for the deep tanks,

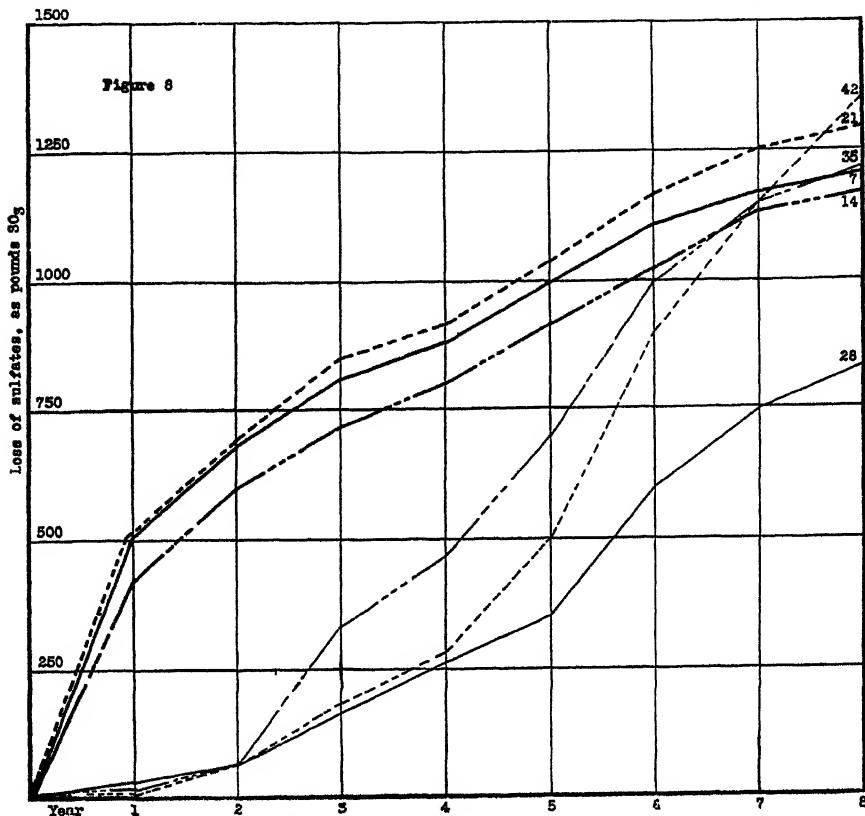


FIG. 8. POUNDS OF SO_3 PER 2,000,000 POUNDS OF SOIL IN LEACHINGS FROM TANKS TREATED WITH MAGNESITE EQUIVALENT TO CaO AS FOLLOWS:

Surface soil	Tank 7—	8 tons	Surface and subsoil	Tank 28—	8 tons
	14—	32 tons		35—	32 tons
	21—	100 tons		42—	100 tons

with the added exception of the limestone treatment, and this exception amounted to 99.0 per cent of the rain water content. The heavy losses from the dolomite shallow tank represented an amount equivalent to 203.7 per cent of the rainfall sulfur.

Expressed in relationship to the amount of SO_3 found in the surface soil, the seven treatments other than CaO caused sulfate leachings of 54.3–98.9

per cent of the amount originally contained in the surface soil. These same six treatments gave sulfate losses ranging from the limestone minimum of 20.8 per cent to the $MgCO_3$ maximum of 35.0 per cent of that possible where the leachings passed through both soil and subsoil.

The amounts of sulfates leached from the surface soil were 3.46, 1.45, 3.20, and 3.14 times the sulfur impurities of the treatments for MgO , $CaCO_3$, $MgCO_3$, and magnesite, respectively. Corresponding respective multiples of 4.50, 1.28, 3.70, and 2.99 were found for the deep tanks. Most probably because of the larger sulfur content of the dolomite, the outgo of sulfates from this treatment was approximately one-fourth of that carried by the addition, in the case of the shallow tank, and approximately one-fifth in the case of the deep tank.

In spite of the magnitude of the SO_3 leachings which passed from the dolomite, they were equivalent to only 17.6 per cent of that available for the shallow tank and but 11.1 per cent for the deep tank, because of the large amount of sulfur added to that of soil and precipitation through the sulfur content of treatment. The other two native materials, the precipitated carbonates of calcium and magnesium and magnesium oxide, induced surface-soil losses ranging between 32.3 per cent and 41.0 per cent of the total of all sulfur sources for $CaCO_3$ and $MgCO_3$, respectively. The corresponding range for the subsoil tanks was from the minimum of 16.9 per cent in the case of $CaCO_3$ additions, to 26.8 per cent in the case of the MgO treatment.

RELATION OF 8-YEAR TOTALS OF OUTGO TO SOURCE OF SULFUR, AS INFLUENCED BY RATE OF TREATMENT

Periodicity of sulfate leaching has been considered in the discussion of the influence of each treatment at the three rates. The divergences between the initial activity and that exerted through the remaining seven years have been shown for each addition at each of the three rates. This discussion will deal with the proportional relationships between the aggregate losses for the 8-year period and the amounts of sulfur available from soil, treatment-impurities, and rainfall.

Burnt lime

Since the outgo of sulfates from the surface soil decreases with increase in treatment, with constant initial soil content and precipitation, and with no sulfur added by the oxide, it follows that the percentage relationship of outgo also decreases with increased rates of application. There is a corresponding per cent decrease when the diminishing surface-soil losses are calculated as fractions of the constant total of all sources of sulfur. The total sulfate outgo from the deep 8-ton tank is almost equivalent to that from the surface soil alone; hence the per cent loss drops from 52.1 to 20.3 of the combined sulfur stores of soil and subsoil. With a distinct decrease in the SO_3 leachings through the subsoil from the 32-ton addition, and the addi-

tional sulfur content of the subsoil, the per cent of the possible drops to the low figure of 6.0. But in the case of the 100-ton addition, the burnt lime has either carried through more of the rain water sulfates or forced the liberation of sulfates already held as such, or else it caused the generation and liberation of additional sulfates from the subsoil. Hence, the augmented amount represents 11.7 per cent of the original sulfur content of soil plus subsoil.

Expressed as fractions of the sulfur content of rain water collections, the SO_3 losses from surface soil show a progressive decrease in per cent—107.3, 75.6, and 24.9, respectively, for the 8-, 32- and 100-ton additions. The SO_3 forced through the subsoil by the 8-ton addition represents the nearest approach to the amount of sulfur brought down by rainfall. That which passed from the 100-ton subsoil tank amounted to a little more than one-half of the amount derived from rainfall. A still smaller amount, about one-fourth of that of the rain water, came through from the soil-subsoil tank which received burnt lime at the 32-ton rate.

Magnesium oxide

The MgO additions of 8, 32 and 100 tons were responsible, respectively, for sulfate leachings equivalent to 52.7, 56.8 and 61.1 per cent of the soil's initial sulfur content. With no great variation in amounts of sulfur lost from the surface soil, treated at the three rates, and with increasing amounts carried as impurities, the factors for outgo-to-treatment relationship decreased with increasing treatments. With uniformity in sulfate losses from the surface soil for the three rates and the approximation in amounts of sulfur available from all sources for each rate, there followed a uniform relationship of outgo-to-source, approximately 36 per cent.

The sulfate losses of 1150, 1310, and 1685 pounds from the deep tanks treated at the rates of 8, 32, and 100 tons, amounted to 23.5, 26.8, and 34.5 per cent, respectively, of the initial sulfur content of soil plus subsoil. Likewise, the increasing proportions of outgo to the totals available from all sources, 19.3, 21.7, and 26.8 per cent, were induced, respectively, by the 8-, 32- and 100-ton treatments. The factors of outgo-to-impurities for the deep tanks decreased with increasing rates of treatment—38.33, 10.92, and 4.50 for 8, 32 and 100 tons, respectively.

Each MgO addition caused the surface soil to yield sulfates in excess of the amount carried by rainfall, the per cent relationships increasing with intensity of treatment. The same as to excess of leachings over rainfall content and order of per cent relationships held true for the deep tanks. Each deep-tank total, however, was greater than that of the corresponding shallow tank, establishing the fact that MgO effected a derivation of sulfates from both soil and subsoil.

Calcium carbonate

Each of three shallow tanks gave a sulfate outgo close to 60 per cent of the original sulfur content of the soil. The sulfate losses from the 8-, and 32-ton additions were closely approximate, and somewhat less than the outgo from the 100-ton-equivalent addition. The outgo-to-total-source relationship and the impurity factors decreased with increase of treatment. Since the sulfate losses did not increase consistently with increase in treatment, the relation between outgo and rainfall sulfates also failed to show per cent increase with increased applications.

The sulfate leachings from the deep tanks approached those from the shallow tanks for the 8-ton and 100-ton additions but were decidedly less for the 32-ton treatment. As stated this relationship holds not only for sulfates, but for total calcium. The largest proportion of the aggregate sulfur stores was carried through the subsoil by the 8-ton treatment and the smallest by the 32-ton addition.

Magnesium carbonate

With increase in treatments, magnesium carbonate caused increases in per cent losses of sulfates from the surface soil. The percentage relationship between sulfate leachings and rainfall sulfur increased with increase in $MgCO_3$ additions for both shallow and deep tanks, each outgo being in excess of the amount brought down in rain water. The impurity factors decreased for both depths with increase in treatment. The sulfate outgo from the shallow tanks was close to 40 per cent of the total available sulfur.

With increase of treatment from 8 to 32 tons, there occurred an increase in percentage relationship of deep-tank sulfate losses to the aggregate amount carried by soil and subsoil. The relationship was quite close, however, for the 32- and the 100-ton additions. The 8-ton rate caused an SO_3 loss about one-fifth of the aggregate of all sulfur supplies, while losses of approximately 27 per cent came from both the 32-ton and 100-ton additions.

Limestone

With the maximum from the 8-ton addition and the minimum from the 32-ton addition in the shallow tanks, each limestone treatment caused a sulfate loss of more than 50 per cent of that possible from the soil. The same order held for relationship of sulfate outgo to rainfall sulfur. In terms of per cent of the aggregate of available sulfur both 8 and 100 tons showed losses greater than the loss from the 32-ton treatment.

The sulfates passing through the subsoil from this treatment are expressed as 17.4, 19.2, and 20.8 per cent of the sulfur carried by both soil and subsoil, in the order of 32-, 8-, and 100-ton treatments. The same order prevails in the losses of 14.4, 15.7, and 17.2 per cent of the respective aggregates of all sources of sulfur.

Dolomite

Increase in the dolomite treatments caused the surface soil to suffer increased losses, 60.0, 67.4 and 98.9 per cent of the amount originally present, having come from the three respective rates. The same holds true as to relationship to the constant amount of rain-water-sulfur content. The 100-ton addition is the only one of 46 tanks which gives a sulfate outgo more than double the amount precipitated by rainfall. The order of per cent relationship is reversed, however, when the actual amounts of sulfur losses are calculated on the basis of aggregate of sulfur supplies, because of the increasing amount of sulfur added as treatment impurities. The factors which express ratio between outgo and impurities decrease with increase in addition.

The ratio of sulfate outgo to combined sulfur content of soil plus subsoil increases with increase of treatment in the deep tanks. The sulfate content of the leachings is less than that of the rainfall in the case of the 8-ton deep tank, but greater for both the 32- and 100-ton rates, the heaviest treatment giving the larger excess. Expressed as per cent of the total available sulfur, the deep tanks give practically the same figures for the 8-, 32-, and 100-ton additions, although the actual amount of sulfate outgo from the latter addition is about twice that from either of the other two. This relationship obtains in spite of the fact that the maximum sulfate came from the 100-ton incorporations, because of the larger residual of unoxidized sulfide impurities.

Magnesite

Increase in magnesite additions did not cause a consistent increase in the fraction of surface-soil sulfur, nor that of rainfall sulfur, which appeared in the leachings. Each of the shallow magnesite tanks lost about 36 per cent of the potential sulfates from soil, treatment, and precipitation.

The 8-ton magnesite addition forced a sulfate loss from the deep tank of about one-sixth of that available from both soil and subsoil and but 79.2 per cent of the sulfate content of the rainfall. The same treatment induced a loss of SO_3 equivalent to only 13.9 per cent of the sulfur derived from all four sources. Both the 32- and 100-ton additions caused a sulfate movement through the subsoil of about one-fourth of the sulfates possible from the stores carried by both surface soil and subsoil and about 20 per cent more than that precipitated by rain. Coincident with the increase in rate of treatment, there occurred a decrease in the factors which expressed the relation between outgo and actual amounts of sulfur added through treatment impurities.

THE OXIDATION OF ZINC SULFIDE CARRIED BY DOLOMITE

In noting the fact that the dolomite treatment was more active than limestone and magnesite in accelerating the outgo of sulfates from the shallow tanks, mention was made of the sphalerite content of the dolomitic limestone.

It was also observed that this disparity in outgo increased with increase in rate and that the maximum of all sulfate leachings came from the 100-ton addition of dolomite. It was assumed that the excesses from the dolomite were due to the oxidation of the zinc sulfide carried by the dolomite. Such oxidation was assumed to be attributable to both chemical and bio-chemical activities. Since the preparation of this manuscript an article bearing upon sphalerite oxidation has been contributed by Rudolfs and Helbronner (9). These workers state: "Apparently as the result of chemical reactions a small amount of zinc sulfide was converted into zinc sulfate" and "However, the inoculated cultures made far more zinc sulfate than the uninoculated mixtures; ". They further found a steady increase in relative acidity, fluctuations in pH values, and no inhibition from the increased concentrations of sulfification end products. In our own results of medium has always been alkaline for each of the three additions because of the excess of dolomite. Therefore, while the sulfifying organisms may best function in an acid medium, it must be concluded that they also function in one of alkaline reaction, if the excesses of sulfates derived from the dolomite treatments are to be considered as having been generated in the main by bacterial action. The sulfate leachings from the dolomite treatments in the shallow tanks were 1271, 1428, and 2093 pounds of SO_3 as the totals for 8 years from the 8-, 32-, and 100-ton additions, respectively. These three amounts were derived from a soil and rainfall constant of 3149 pounds of SO_3 plus 701, 2804, and 8763 pounds of SO_3 supplied by the respective dolomite additions. The sulfate losses from the surface soil were generally more extensive during the first two years. The losses for the first four years were 66.7, 64.3, and 55.1 per cent of the respective 8-year totals for the additions at the rate of 8, 32, and 100 tons. It can not well be assumed, however, that the major fractions of the sulfate leachings were derived from the sphalerite content of the finely ground dolomite unless the dolomite were considered as differing from the other carbonates and as having no effect upon the oxidation of native soil organic sulfur. For both the precipitated and the native forms of calcium and magnesium carbonates caused a marked acceleration in the outgo of sulfates and a large part of each increase was necessarily derived either from the native sulfur content of the soil or from the rainfall, or from both. When the activities of the organisms responsible for the sulfification of the sphalerite are established for alkaline calcic-magnesian media containing also neutral calcium and magnesium salts, it will be easier to draw conclusions as to the relative proportions of chemical and bio-chemical oxidations of sphalerite which were responsible in part for the dolomite-induced sulfate leachings reported in this study.

SUMMARY

An 8-year study of annual sulfate leachings from tanks containing surface soil and surface soil plus subsoil, as influenced by nine different calcic and magnesian materials in different amounts, was carried out by the use of forty-six field lysimeters.

Comparison of treatments disregarding sulfur sources

At the 8-ton rate, all seven materials, CaO, MgO, CaCO₃, MgCO₃, 100-mesh limestone, dolomite, and magnesite, materially increased the loss of sulfates from the surface soil. Compared with initial annual outgo, there was a distinct diminution in all losses from the surface soil after the first year. The losses from the treated tanks, however, continued to be greater than those from the control. Only fractions of the increases of the initial year passed through the subsoil, but represented distinct increases over the meager leachings through the subsoil of the control. The tendency of the subsoil losses was to increase from minimum initial outgo, the amount of increase depending upon the solubility of the alkali-earth addition. The differences between the 8-year outgo of SO₄ from surface soil and from suriace soil plus subsoil were greatest in the case of the native carbonate treatments.

At the 32-ton rate the distinctly depressive influence of CaO is shown in contrast to the activating influence of MgO and the carbonates. The MgO and MgCO₃ admixtures were the most active at first. The sulfate losses from the surface soil decreased for all treatments, save CaO, after the initial year. The losses of the second and third years and many of those of the succeeding years, were, however, still in excess of losses from the control tank. The sulfate losses from the subsoil tanks were greatest for the MgO and MgCO₃ treatments during the second and third years. The smaller losses from less soluble materials and CaO did not become maximum until the third year, or the fifth year, and in three cases, even later. The 8-year totals from surface soil and from subsoil tanks were less for the CaO treatment than for the others. The relationship between the surface-soil 8-year totals and those from the soil-subsoil were governed by the solubilities of the several additions. Wollastonite was found to increase the losses much more than serpentine.

At the 100-ton rate, CaO was found to be exceedingly effective in stopping losses from the surface soil, but after the fourth year the heavy addition became active in forcing sulfates from the subsoil zone. All other additions increased the surface soil losses to excessive amounts during the initial year, the MgO and MgCO₃ treatments again being most active in this regard. Even with a decided fall-off during the second and third years, the losses during each of these two years were still largely in excess of the loss from the surface soil control. The maximum surface-soil outgo for the 8-year period was caused by dolomite which materially supplemented the sulfur stores available for oxidation because of its content of sphalerite.

The MgO and MgCO₃ treatment were again the first to force surface-soil sulfates through the subsoil, the largest amounts coming during the third year. The less soluble materials showed increased losses from the subsoil during the fifth and sixth years and even through the seventh year. The more penetrating MgCO₃ and MgO additions were responsible for large losses sulfates from the subsoil zone, and thus caused soil-subsoil totals in excess

of those from the corresponding surface soil. The remaining four of the six more active materials caused larger 8-year losses from the surface soil than from the surface soil plus subsoil.

The influence of magnitude of treatment was found to vary. Increase in applications of burnt lime was followed by progressive depression of surface-soil sulfate outgo, but only the heaviest application depressed the total below that of the control. Compared with the increases from the other six oxide and carbonate additions in the deep tanks, increase in amounts of lime brought increased, though not progressive, depression. But in spite of this effect the sulfate outgo for each treatment was largely in excess of that of the subsoil-tank control.

Increased treatments of MgO and MgCO₃ caused progressive increases in both initial and total sulfate losses from the surface soil. The same held true in regard to soil-subsoil losses.

The chemical and biochemical factors responsible for the depressive action of CaO were considered in connection with calcium hydroxide concentrations of leachings and the solubility of freshly precipitated CaSO₄ in such concentrations.

No consistent increase in sulfate outgo from the surface soil resulted from increase in rates of treatment of CaCO₃, limestone, or magnesite, but increased loss of sulfates, with increased treatments of dolomite in both surface soil and subsoil tanks was probably due to increasing amounts of sphalerite.

The sulfate increases in the subsoil leachings were found to be more dependent upon the solubility than quantity of the alkali-earth additions and ran parallel with increased concentration of the applied base in leachings. While increased MgO, MgCO₃, and dolomite additions gave decided progressive increases in total SO₃ lost from the subsoil, the same did not hold for CaCO₃ and limestone. Although a material increase in sulfate losses followed the increase of magnesite from 8 tons to 32 tons, little additional outgo resulted in the further increase to 100 tons.

The systems MgCO₃-MgSO₄-H₂O and CaCO₃-CaSO₄-H₂O were affected differently by the treatments with MgO, CaCO₃, and MgCO₃ and they differed in rapidity of outgo from the subsoil. Greatly increased sulfate leachings and increased alkalinity were induced first by the 32-ton-equivalent additions of both MgO and MgCO₃, though the totals came in order of treatment. But the totals of both sulfates and calcium were less from the 32-ton CaCO₃ treatment than from either 8- or 100-ton additions.

Effect of treatments as related to sources of sulfur

Relationships were calculated for each total outgo to each of the several sources of sulfur; viz., soil, soil and subsoil, treatment impurities, and rainfall. Except CaO at 32- and 100-ton rates, every treatment at each rate caused a loss of more than one-half of the original sulfur content of the surface soil. With the same exception, all treatments caused losses in excess

of the rainfall sulfur. All treatments at the 8-ton rate induced sulfate losses approximating 35 per cent of the sulfur available from all sources. The same was true of all surface-soil losses from the 32- and 100-ton additions of MgO, CaCO₃, MgCO₃, limestone, and magnesite. Expressed as per cent of the total sulfur available, the sulfate leachings from the surface soil tanks decreased with increase in treatments of both CaO and dolomite. The burnt lime caused actual as well as per cent decreases. But in spite of a marked progressive increase in outgo parallel with increase in dolomite treatment, the outgo appears as a low per cent of the total available sulfur because of the augmented sulfur supply and unoxidized residues of sphalerite impurities.

The sulfur loss from each of the seven treatments, at each rate was less than the amount originally present in the soil plus subsoil. With the exception of CaO and limestone at all rates, dolomite and magnesite at the 8-ton rate and CaCO₃ at the 32-ton rate, each of the seven materials caused subsoil sulfate leachings in excess of the amount of SO₃ carried by the rainfall. The respective relationships between subsoil losses and totals from all sources may be considered best in detail by reference to the last column of table 8.

It was shown that unaltered subsoil stopped large amounts of sulfates and that the influx of calcium and magnesium salts served to diminish or even overcome this property and in some cases to push sulfates through the subsoil.

The value of parallels of tanks with and without subsoil is emphasized in the determination of periodicity and magnitude of sulfate generation in the surface soil; the increased or decreased tendency of the subsoil to permit passage of sulfates as a result of treatment; the subsoil zone as a source of engendered or liberated sulfates; and attainment of balance between the several systems involved in the sulfate concentrations of the leachings.

The sulfate sulfur leached from the untreated soil was less than the amount brought to it by rainfall.

The oxidative processes responsible for the generation of sulfates from zinc sulfide were mentioned and assumed to be of both chemical and biochemical nature, until more data are at hand relative to biological activities in alkaline calcium-magnesium media.

The treatments heavier than the 8-ton equivalent rate may be considered primarily as of academic interest, in showing the divergent effects induced by the several materials applied. But the data from the 8-ton additions may be construed not only as showing the divergent influences of treatment, but also as indicating that the injudicious use of liming materials may rapidly impair the supply of sulfur carried by the surface soil, particularly where the supplementary supplies derived from rainfall are meager in quantity.

REFERENCES

- (1) CAMERON, F. K., AND BELL, J. M. 1906 The system lime, gypsum, water, at 25°. *In* Jour. Amer. Chem. Soc., v. 28, p. 1220, 1222.
- (2) LYON, T. L., AND BIZZEL, J. A. 1918 Lysimeter experiments. N. Y. (Cornell) Agr. Exp. Sta. Mem. 12.
- (3) LYON, T. L., AND BIZZEL, J. A. 1921 Lysimeter experiments. II. N. Y. (Cornell) Agr. Exp. Sta. Mem. 41.
- (4) MACINTIRE, W. H. 1915 Two equipments for investigation of soil leachings. Univ. Tenn. Agr. Exp. Sta. Bul. 111.
- (5) MACINTIRE, W. H. 1916 Factors influencing the lime and magnesia requirements of soils. Univ. Tenn. Agr. Exp. Sta. Bul. 115.
- (6) MACINTIRE, W. H. 1919 The carbonation of burnt lime in soils. *In* Soil Sci., v. 7, no. 5, p. 370-379, 449.
- (7) MACINTIRE, W. H., WILLIS, L. G., AND HOLDING, W. A. 1917 The divergent effects of lime and magnesia upon the conservation of soil sulfur. *In* Soil Sci., v. 4, no. 3., p. 231.
- (8) MACINTIRE, W. H., AND YOUNG, J. B. 1922 Sulfur, calcium, magnesium and potassium content and reaction of rainfall at different points in Tennessee. *In* Soil Sci., v. 15, p. 205-227.
- (9) RUDOLFS, W., AND HELBRONNER, ANDRÉ. 1923 Oxidation of zinc sulfide by micro-organisms. *In* Soil Sci., v. 14, no. 6, p. 462.
- (10) SEIDELL, A. 1907 Solubilities of inorganic and organic substances, p. 91, 99. D. Van Nostrand Company, New York.

SOIL ACIDITY, AN ECOLOGICAL FACTOR¹

ARTHUR PIERSON KELLEY

University of Pennsylvania

Received for publication May 17, 1923

INTRODUCTION

Since colorimetric methods were developed for the study of soil extracts there has been an increasing number of observations on the relation of the hydrogen-ion concentration of the soil extract to plant distribution. The general conclusion resulting from these studies has been that a soil of a particular locality has a more or less definite pH value and that plants found upon this soil are frequently those having a preference for that hydrogen-ion concentration.

These studies have been made frequently by testing the surface soil or that about living roots plucked from the soil. It seemed desirable to make a more intensive study of a particular region through a considerable length of time, taking into consideration the pH values of the subsoil and their relation to root distribution.

Subsoil acidity has not been without investigators. Wherry (13), working at Millsboro, Delaware, in March 1919, found that in digging down into sand beneath upland peat the acidity decreased markedly. Two years later Arrhenius (2), making borings about Bahtim and Giza in Egypt in some cases to a depth of 300 cm., found that the surface soil was alkaline but that the alkalinity decreased with depth; finding at Bahtim, however, an increase in pH values from surface to a certain depth followed by a decrease. Salisbury (10), in England, has also found a decrease in acidity of the subsoil of woodlands.

SOILS AND METHODS OF TESTING

A convenient locality was found in Chester County, Pennsylvania, about the village of Paoli. Within a radius of five miles there are five soil types with a number of diversified phases; Hagerstown (limestone), Chester (granitic), Manor (schistose), Dekalb (sandstone) and Conowingo (serpentine). A description of these soils and their location will be found in an earlier paper (6). Comparable areas were selected, representing as far as possible the average condition of that soil type and having as far as possible among themselves the same degree of slope, drainage and exposure. A large proportion of the tests were made in wooded regions which were as nearly in an undisturbed condition as could be found, while many tests were made in cultivated fields as well.

¹ A thesis presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Work was begun in November 1920. Originally only the surface soil was tested, by the colorimetric method described by Wherry (12). In the summer of 1921 it was decided to make careful tests on the subsoil. The soil auger used, consisted of a 1.5-inch wood auger the shaft of which was threaded and fitted to 50 cm. joints of gas-pipe and a handle. This could be carried conveniently in the field and could be operated to a depth of two metres, though this depth was not found except in Hagerstown loam.

In boring, care was taken that the samples should not be contaminated by soil of higher levels. A bit of the core from successive 15-cm. levels was pressed into a glass test-tube 100 x 15 mm. to a height corresponding to that of 5 cc. of water; the tube was corked and carried to the laboratory. Here distilled water (conductivity 2×10^{-6}) was added to a level equivalent to that of 15 cm. of water; the soil and water were then thoroughly stirred with a clean glass rod, and the suspension was allowed to settle, requiring usually from two to twelve hours. The entire interval between taking the sample and testing was seldom more than twenty-four hours.

Clear extracts could then be tested directly, using 1 cc. of the extract and comparing with standards as described by Clark and Lubs. Since the extracts were frequently turbid, a comparator was constructed by which the turbid extract might be compared with the standard which was screened by a similar turbid extract, viewed by electric light screened by blue glass. When very turbid the extract was diluted with distilled water to two or three times its volume, giving but a small error.

TABLE 1
Relation of productivity to soil reaction

SOIL TYPE	CHARACTERIZATION BY SOIL SURVEY	AVERAGE REACTION
Hagerstown.....	"exceptionally well adapted to crop production"	pH 6.92
Chester.....	"well adapted to crop production"	6.53
Manor.....	"of considerable less value than Chester"	6.15
Dekalb.....	"not very productive"	5.71
Conowingo.....	"very poor"	5.38

RESULT OF SOIL TESTS

Surface soil tests had shown that a general average pH could be assigned to comparable areas of each loam, and these are given in table 1, together with a characterization of each soil made by the United States Department of Agriculture soil survey in 1906 (15). Correspondence between degree of fertility and pH value is evident.

Results of boring tests are given in table 2, in which the serial number of the test is given in the left-hand column, the depth in centimeters at the top and the average acidity at the bottom. Tests were not made closer than pH 0.1. All tests were made colorimetrically and have not been checked with the hydrogen electrode. Tests on Dekalb and Conowingo loams may be somewhat in error because indicators used with these soils were methyl red and cresol purple, which indicators are often not in agreement. Two indicators were always employed in testing and in some doubtful cases three.

Relations between average values determined from table 2 are made more evident by figure 1. It is seen at once that in most cases the curve does not

TABLE 2
Reaction of soil types studied

ARTHUR PIERSON KELLEY

TABLE 2—Continued

SERIAL TEST NUMBER	REACTION AT VARIOUS DISTANCES FROM SURFACE								SERIAL TEST NUMBER	REACTION AT VARIOUS DISTANCES PRO SURFACE							
	Surface	15 cm.	30 cm.	45 cm.	60 cm.	75 cm.	90 cm.	105 cm.		Surface	15 cm.	30 cm.	45 cm.	60 cm.	75 cm.	90 cm.	105 cm.
	pH	pH	pH	pH	pH	pH	pH	pH		pH	pH	pH	pH	pH	pH	pH	pH
<i>Chester loam—Continued</i>																	
1419	6.3	6.3	6.2	6.0	6.0				352	5.4	5.2	5.4	5.4	6.0			
1484	7.0	6.8	6.8	7.0	7.0				472	5.8	5.8	6.0	6.2				
1489	7.0	...	6.8	6.8	7.0				476	5.4	5.2	5.2	5.2	5.2			
1494	7.0	6.8	6.9	6.9	7.0				487	5.9	6.2	6.4	6.4	6.4			
1568	6.8	6.2	6.7	6.8	6.8				492	6.0	6.5	6.4	6.2	6.0			
1573	7.0	6.6	6.5	6.7	6.8				710	6.1	5.7	5.6	5.6	5.8	5.7	6.0	
1578	6.1	5.8	6.4	6.8	...				717	5.0	...	5.2	5.1	5.2	5.5		
Av.	6.5	5.9	6.1	6.2	6.2	6.2	6.2	6.2	723	5.0	5.6	5.4	5.2	5.2			
<i>Manor loam</i>																	
370	...	5.2	6.2	6.6	6.4				785	5.7	5.6	5.7	5.7	5.6	5.6		
375	6.0	6.2	6.2	6.6	6.4	6.6			792	5.6	5.4	5.4	5.8	5.8			
381	6.1	5.6	6.7	6.8	7.0	6.9	6.8		760	5.7	5.2	5.0	5.0	5.0	5.0	5.0	
388	...	5.2	5.0	5.0	5.0	5.0	5.0		767	5.6	5.0	5.0	5.0	5.4	5.7	5.6	
395	...	5.2	5.5	5.1	5.2				774	5.9	5.4	5.6	5.4	5.8	5.8	6.0	
400	...	4.7	4.7	5.0	5.0	5.2	5.4		781	5.6	5.4	5.6	5.7				
676	7.0	6.2	6.5	6.8	6.8	6.8	6.8		897	5.4	5.4	5.6	6.0	6.5			
686	6.8	5.6	6.6	6.8	6.8				902	5.3	5.4	5.9	6.1				
867	6.5	5.7	6.5	6.5	6.6				906	5.8	5.4	5.6	5.7	6.1			
872	6.4	5.8	6.6	6.8	6.5				911	6.1	6.6	6.6	6.4				
919	7.0	6.1	5.9	6.3	6.5				929	5.8	5.6	5.6	5.7				
924	7.0	6.1	5.9	6.3	6.5				934	5.4	6.0	6.2	6.4	6.5			
1094	5.2	5.0	5.0	5.1	5.1				939	6.0	6.0	5.9	6.0	6.0			
1099	5.8	5.2	5.0	5.0	5.0				944	5.8	6.0	5.0	5.6	5.7			
1106	5.6	5.5	5.7						954	5.4	5.4	5.2	5.2	5.2			
1114	6.2	5.8	6.4	6.5	6.5				959	5.8	5.8	6.0	6.0	6.0			
1119	6.6	6.5	6.0	6.0	6.4				963	5.7	5.4	5.3	5.3	4.9			
1134	5.1	4.8	4.9	4.9	5.2				968	5.8	5.4	5.8	6.1				
1301	5.4	5.6	6.1	6.1	6.2				1207	6.0	6.0	6.3	6.4	6.2			
1306	5.4	5.1	5.3	5.4	5.5				1212	6.3	6.1	6.3	6.4	6.4			
1311	5.6	5.5	5.7	5.9	6.1				1311	5.6	4.9	4.9	5.2	5.2			
1366	5.8	5.4	6.0	6.0	6.0				1356	5.6	5.2	5.0	5.1	5.2			
1371	5.8	...	6.5	6.5	6.5				1361	5.6	5.4	5.4	5.8	5.6			
1376	6.1	6.1	6.0	6.0	5.8				1396	5.7	5.3	5.3	5.4	5.6			
1454	6.7	6.2	6.6	6.9	6.8				1401	5.7	5.3	5.3	5.3	5.5			
1459	6.6	6.2	6.9	6.9	6.8				1406	6.1	5.4	5.4	5.5	6.1			
1464	6.6	6.4	6.8	6.8	6.8				1429	6.1	5.4	5.4	5.7	5.7			
1579	6.8	6.4	6.6	6.6	6.8				1434	6.1	6.4	5.4					
1584	6.6	5.8	6.0	6.8					1593	5.4	5.8	6.0	6.2	6.4			
1588	5.8	6.0	6.0	6.2	6.4				1598	6.2	6.4	6.4	6.6	6.6			
Av.	6.1	5.7	5.8	6.1	6.2				1603	5.8	6.0	5.6	6.4	6.6			

SERIAL TEST NUMBER	REACTION AT VARIOUS DISTANCES FROM SURFACE							
	Surface	15 cm.	30 cm.	45 cm.	60 cm.	75 cm.	90 cm.	105 cm.
	pH	pH	pH	pH	pH	pH	pH	pH
418	4.6	4.8	5.0	5.8				
422	4.6	4.4	5.6	5.8				
549	5.4	5.4	5.6	5.8	6.2			
557	5.4	6.2	6.1	6.2	6.4	6.4		
530	5.6	5.6	5.8	6.1	6.2	6.1		
541	5.6	5.6	5.8	6.1				
549	5.4	5.4	5.6	5.8	6.2			
557	5.4	6.2	6.1	5.8	6.4	6.4		
632	5.1	5.0	5.2	5.2	5.7	5.8		
639	5.4	4.9	5.2	...	5	8	6.0	
646	6.0	5.8	5.8	5.8	6.2			
653	5.8	5.4	6.2	6.4	6.4	6.6		
659	6.0	6.0	6.4	6.4	6.1	6.1		
847	5.0	5.6	5.7	5.8	6.0			
857	5.0	5.4	5.6	5.8	6.2			
1139	5.2	5.6	6.0	6.5	7.0			
1144	5.4	5.8	5.8	6.0	6.2			

Conowingo loam

SERIAL TEST NUMBER	REACTION AT VARIOUS DISTANCES FROM SURFACE							
	Surface	15 cm.	30 cm.	45 cm.	60 cm.	75 cm.	90 cm.	105 cm.
	pH	pH	pH	pH	pH	pH	pH	pH
1149	5.8	6.0	6.0					
1152	4.8	5.0	6.0	6.5	6.2			
1157	5.0	4.8	5.0	5	6.0			
1162	5.6	5.6	5.8	6	0			
1166	6.1	5.7	6.5	6.5	6.5			
1171	5.2	5.6	5.8	5.6	6.0			
1233	5.4	5.8	6.0	6.0	6.3			
1238	6.1	4.4	5.1	5.3	5.3	5.5		
1294	5.2	...	5.3	5.5				
1469	5.4	5.6	5.8	5.8	5.8			
1474	5.4	5.0	5.6	5.8	5.8			
1608	5.4	6.2	6.4	6.4	6.4			
1613	5.8	5.9	6.0	6.4				
1617	4.8	5.4	5.8	6.2	6.4			
Av.	5.3	5.4	5.7	5.9	6.5			

Conowingo loam—Continued.

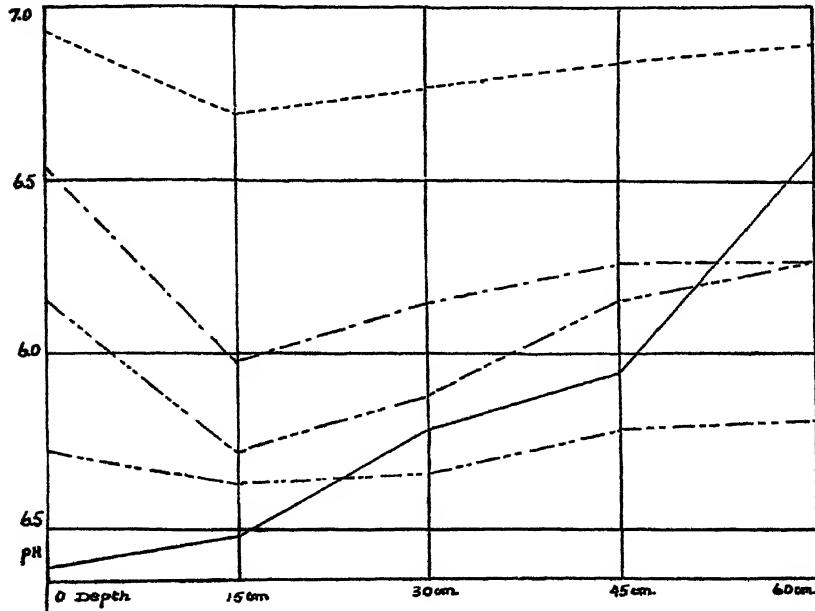


FIG. 1. GRAPHS SHOWING VARIATIONS IN ACIDITY WITH DEPTH

- Hagerstown Loam.
- Chester Loam.
- Dekalb Loam.
- Manor Loam.
- Conowingo Loam.

show a steady rise from the acid side towards neutrality as most previous work would indicate but that there is a drop in pH to about 15 cm., rising then at lower levels towards the neutral point,—a type of curve found by Arrhenius at Bahtim, Egypt. This drop is small in limestone soil; in the others we find that the successive curves between 0–15 cm. describe as it were an arc—somewhat like an opening fan—as the surface soil acidity increases faster than that of the subsoil, until the curve shows a steady decrease from surface downwards. In all cases there is a rise of the pH value at lower depths towards neutrality; this is markedly so in Conowingo. A general statement, then, regarding subsoil acidity can not be made for all but for particular kinds of soil, except that at lower depths the reaction approaches neutrality.

MONTHLY SOIL TESTS

Values obtained from monthly tests made in the same locality for one year are given in table 3. The reader will note that there is no fixed pH value for any particular portion of soil, and that the change from the mean is not large. It amounts at times, however, to pH 1.0 during the growing season, in the subsoil as well as at the surface, hence the plants growing in these places can not be appreciably injured by small variations in acidity.

It will also be seen that during the late summer, from July to October, there is a continual increase in the acidities recorded, except in Dekalb and Conowingo for August (these tests were made one week later than the others in that month, after a rain storm), and in Manor for September. All tests in September were made within two days, after a heavy rain-storm by which Manor loam seems to have been differently affected. The three months on the whole were marked by a long-continued drought; with coming of late autumnal rains the acidity decreased. Then, with coming of freezing, the pH values was again lowered to rise once more on thawing; we see in Hagerstown for February, while still frozen, a lower pH while the other soils had thawed.

Under field conditions drying is apparently often accompanied by increased acidity, but not invariably; thus in Conowingo loam tests made after a heavy rain showed increased acidity, whereas drying in the next month to a pulverulent powder was accompanied by a decreased acidity. These conclusions might be compared with those found by Burgess (3) viz., that acid soils were little changed in acidity by drying in the laboratory.

DISCUSSION OF RESULTS OF SOIL TESTS

The significance of the type of curve found is not apparent. From studies made in woodlands one might consider that decay and leaching of organic acids from leaves and plant debris might cause an acid condition in the subsoil while the salts remaining at the surface might cause a lessened acidity (5). A recent paper (9) attempts to show that facies of a formation determine the reaction of the soil upon which they grow by the different amounts of acid-formers liberated from their decaying leaf-litter.

But the same type of curve is found under old sod where there should be but little leaching, and in cultivated fields where there should be almost none.

TABLE 3
Results of monthly tests, April, 1922–March, 1923

MONTH	REACTION AT VARIOUS DISTANCES FROM SURFACE					MONTH	REACTION AT VARIOUS DISTANCES FROM SURFACE				
	Sur- face	15 cm.	30 cm.	45 cm.	60 cm.		Sur- face	15 cm.	30 cm.	45 cm.	60 cm.
	pH	pH	pH	pH	pH		pH	pH	pH	pH	pH
<i>Hagerstown loam</i>											<i>Manor loam—Continued</i>
April.....	7.0	6.9	6.7	6.6	6.8	December.....	5.5	5.3	5.7	5.8	5.9
May.....	7.0	7.3	7.3	7.4	7.5	January.....	5.9	5.7	6.0	6.0	6.0
June.....	7.0	6.6	6.9	7.0	7.1	February.....	6.6	6.2	6.8	6.8	6.8
July.....	7.0	6.7	7.0	7.0	7.0	March.....	6.4	6.0	6.2	6.4	6.6
August.....	7.0	6.6	6.6	6.6	7.0						
September.....	6.6	6.3	6.3	6.4	6.6						
October.....	7.1	6.8	6.6	7.0	6.9						
November.....	7.3	7.0	7.2	6.9	7.1						
December.....	6.4	6.0	6.0	6.0	6.0						
January.....	7.0	6.8	6.7	7.0						
February.....	6.8	6.8	6.5	6.6	6.6						
March.....	7.0	6.8	6.8	6.8	7.0						
<i>Chester loam</i>											<i>Dekalb loam</i>
April.....	6.2	6.0	6.3	6.4	6.5	April.....	5.8	5.4	5.0	4.8	
May.....	6.8	6.2	6.4	6.5	6.4	May.....	5.6	5.7	5.6	6.0	5.7
June.....	6.0	5.9	6.2	6.6	6.7	June.....	5.4	5.7	5.6	5.4	5.4
July.....	6.6	5.8	6.1	6.0	6.3	July.....	5.7	5.3	5.3	5.3	5.5
August.....	6.6	6.3	6.1	6.4	6.5	August.....	5.8	5.9	5.9	6.0	6.2
September.....	6.0	5.8	6.0	6.0	6.1	September.....	5.6	5.7	5.4	5.6	5.6
October.....	6.8	6.5	6.7	6.8	6.8	October.....	5.9	5.4	5.8	5.7	4.9
November.....	6.7	6.0	6.1	6.2	6.3	November.....	6.1	6.0	6.3	6.4	6.2
December.....	6.1	5.6	5.7	6.3	6.3	December.....	5.6	5.1	5.1	5.3	5.3
January.....	6.4	6.3	5.8	5.7	5.8	January.....	5.7	5.3	5.4	5.4	5.5
February.....	7.0	6.8	6.8	6.9	7.0	February.....	6.1	5.4	5.4	5.6	5.9
March.....	6.9	6.4	6.6	6.8	6.8	March.....	5.8	6.0	6.0	6.4	6.5
<i>Manor loam</i>											<i>Conowingo loam</i>
April.....	6.3	5.4	5.6	5.8	5.8	April.....	5.6	5.7	5.8	6.0	6.2
May.....	May.....	5.5	5.9	5.8	6.0	6.2
June.....	6.2	5.5	6.0	6.1	6.2	June.....	5.6	5.4	5.7	5.7	5.9
July.....	6.4	5.7	6.5	6.6	6.5	July.....	5.0	5.5	5.6	5.8	6.1
August.....	5.6	5.2	5.2	5.0	5.0	August.....	5.4	5.8	5.9	6.2	6.6
September.....	6.2	5.9	6.0	6.2	6.3	September.....	5.1	5.1	5.6	5.9	6.1
						October.....	5.9	6.0	6.6	6.0	6.3
						November.....	5.6	5.8	6.0	6.4	6.5
						December.....	5.4	5.3	5.2	5.4	5.5
						January.....	5.0	4.4	5.2	5.4	5.5
						February.....	5.4	5.0	5.6	5.8	5.8
						March.....	5.2	5.8	6.0	6.3	6.4

Table 4 gives the averages of results obtained from forty series of tests made in open fields immediately adjacent to the wooded areas studied for the soil types, made monthly from July to February inclusive.

The curve might result from chemical reactions and adsorption phenomena so that the actual acidity might not appear at the surface, and in the sub-soil acid salts set free from their adsorbed condition by an excess of organic acids might be gradually neutralized by basic substances arising from below in the ground water.

From a study of the distribution of microörganisms in the soil as given by numbers of workers (7) it seems that in general these are found chiefly in the first 16 cm. of soil, with comparatively few below 90 cm. It would seem also that bacteria, protozoa and some algae are to be associated with a soil reaction near neutrality while fungi are more frequently found under acid conditions. It was shown further by Moore (8) that in some soils bacteria had been found at the surface whereas fungi were in lower levels of the same soil. In the soils studied fungi were practically absent from Hagerstown loam, not uncommon in Chester, becoming very abundant in Conowingo loam where they formed with roots a dense mycorrhizal mass knitting the leaf-litter together. While microörganisms may have no relation to soil

TABLE 4
Average reactions of cultivated soils

SOIL TYPE	REACTION AT VARIOUS DEPTHS FROM SURFACE				
	Surface pH	15 cm. pH	30 cm. pH	45 cm. pH	60 cm. pH
Hagerstown.....	6.84	6.62	6.54	6.68	6.77
Chester.....	6.36	6.06	6.34	6.36	6.44
Manor.....	6.15	5.92	6.11	6.26	6.31
Dekalb.....	5.94	5.85	5.86	6.12	6.25
Conowingo.....	5.84	6.03	6.06	6.40

acidity except as it forms one of the ecological factors to which they are subject, an interesting problem is nevertheless opened for investigation.

RELATION TO ROOT DISTRIBUTION

Soil acidity affects the plant through the roots and study of root distribution is consequently important in any investigation of the effects of hydrogen-ion concentration on vascular plants. There have been excellent works on root distribution, as that of Weaver (11), who traced out entire root systems with the utmost care, finding that herbs and shrubs of the forest floor are relatively shallow-rooted, that almost without exception the bulk of the absorbing system lies within the surface eighteen inches of soil and that even roots of trees have many shallow branches.

The writer has made some observations on roots of woodland species by digging a trench two meters long, a half-meter wide and down to loose rock. Study of tree roots is more difficult in order to make generalizations. Numerous quarries of the region were studied, where freshly loosened faces are con-

stantly exposed, and neatly exhibit the root distribution not only of herbs and shrubs but also of trees. Trees of various species uprooted by wind-storms were also observed. All observations indicated the same general conclusion, that most of the absorbing system of woodland plants is near the surface. It seemed questionable even whether trees in general have deeply penetrating tap-roots, and in two soil types they would be practically impossible since bed-rock occurs within two meters of the surface.

An example of root distribution under "average" conditions (in Manor loam) is shown in figure 2, drawn to scale from a surface exposed by an excavation. Most of the absorbing system is within the first 12 cm. with another stratum from 30 to 70 cm. and only occasional fibrous roots below,

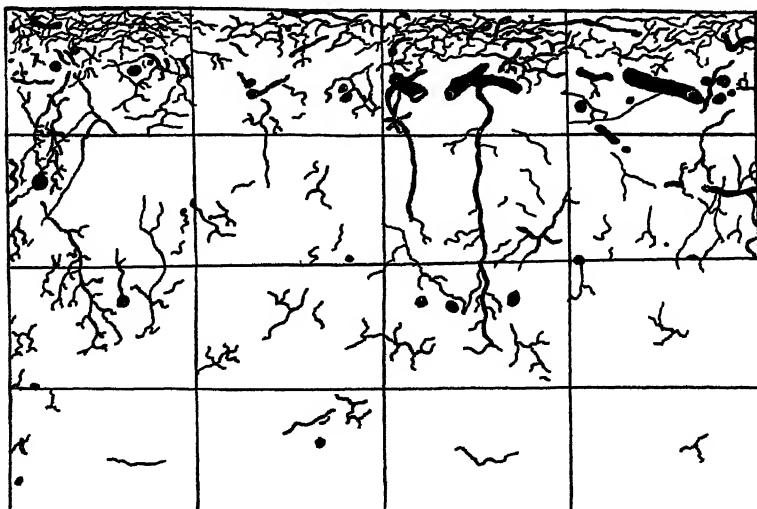


FIG. 2. ROOT DISTRIBUTION IN MANOR LOAM

Scale: 1 mm. = 2 cm.

while there is a layer of conducting roots at 15 cm. Absorbing roots would seem to be associated here with soil nearer neutrality. Dekalb soil is shallower and the root system is more compressed, still more so in Conowingo. In Chester and Hagerstown loams apparently absorbing roots are spread deeper in the soil.

Mycorrhiza were found abundantly in the lower part of the leaf mold and in the soil (of the above example) to a depth of 15 cm. where they formed a network of white hyphal strands. Mycorrhiza were most abundant in Conowingo woodland soil, least abundant in Chester and absent from Hagerstown. Where they were most abundant the reaction curve showed no depression but steady rise from a low pH, a condition found also in sterile pastures.

PLANT DISTRIBUTION

The significance of plants as indicators of soil conditions described by different writers from the beginning of such work has been summarized to 1919 by Clements (4) who has also indicated the relation of various ecological factors to plant species. Of these factors, hydrogen-ion concentration is one. Various factors have been considered as controlling plant distribution; among these relative elevation, degree of shade, slope exposure, soil temperature, soil moisture, soil texture, aeration, carbon dioxide and salt content of the soil, and soil reaction. One has been stressed at one time at the expense of others. In 1920 Arrhenius (1) considered that soil acidity was a primary factor and in 1922 Wherry (14) agreed that soil acidity is of fundamental importance. It would seem that by interaction of many or all of these factors, one of which at some time and in some place may become predominate, there results an ecological environment causing a specific plant association.²

This idea of the soil as "a living thing" has been emphasized by Professor John W. Harshberger, to whom the writer is indebted for advice and help during prosecution of this work.

In studying the ecology of the Paoli region the writer, after familiarizing himself with the flora, undertook quadrat surveys in woods of the various soils. A quadrat of 15 meters was chosen since this size is conveniently measured and a block of four quadrats corresponds roughly to the 100-foot quadrat used by some others. Because the region is undergoing suburban change, woodlands often indicate succession stages and quadrat plottings may show quite different results. A comparison of a number is therefore necessary for an appreciation of the real significance of vegetational distribution on that soil.

Facts as to presence and relative abundance of many species on the soil types studied have already been given (6). It is now desirable to present a more detailed comparison of the consociies.

PLANT DISTRIBUTION ON THE SOIL TYPES

Most productive among the soils, Hagerstown loam is largely under cultivation and presents but few areas of woods on any but rocky ledges. Here *Ulmus americana*³ is the dominant species (with *Acer saccharum* in one region),

² The excellent work of Carsten Olsen in Compt. Rend. Labor. Carlsb., v. 15, no 1, 1923, did not appear in time to be reviewed in this paper. The writer would call attention, however, to emphasis laid upon the necessity of filtration of the soil extract to remove any solid particles which might cause adsorption of the indicator, falsifying the result. But might not the filter paper introduce as serious an error by adsorption? The paper also shows the value of comparing several entirely different soil types, for two similar habitats on one soil type with the same hydrogen-ion concentration may support the same facies, but two similar habitats with the same hydrogen-ion concentration on different soil types may have quite different facies. Hydrogen-ion concentration, then, would not be the controlling factor.

³ All species names are according to the seventh edition of Gray's Manual.

while *Fraxinus americana* is subdominate and such species as *Juglans nigra*, *Fagus grandifolia*, *Quercus rubra*, *Liriodendron tulipifera*, *Platanus occidentalis*, *Prunus Mahaleb* are sparse or may form families. These grow in open formation, often with an overhead draped and luxuriant growth of *Vitis cordifolia* making a deep shade so that but few of the smaller treee are found, as *Celtis occidentalis* and *Prunus virginiana*, while saplings of the trees noted above are frequently killed. *Rhus toxicodendron* grows characteristically over ledges and forms mats of erect branches on open ground. The bush stratum is almost entirely *Benzoin aestivale*, changing to species of *Rubus* where there is an opening permitting light to strike through. Little leaf-mold is present, leaves quickly decay and the soil often becomes dry and pulverulent in late summer. There is a sparse ground cover of *Geum canadense*, *Agrimone hirsuta*, *Solidago ulmifolia*, *Aster cordifolia*, but on moist shaded (usually north-facing) slopes are families of *Polystichum acrostichoides*, *Aspidium marginale*, *Thalictrum dioicum*, *Hepatica triloba*, *Cicimifuga racemosa*, *Cheilidonium majus*, *Dicentra canadensis*, *Dentaria laciniata*, *Osmorhiza longistylis*, *Hydrophyllum virginicum* and *Nepeta hederacea*, though *Stellaria media* frequently forms a wide-spread evergreen mat.

Some of the ledges are occupied by a dense growth of *Juniperus virginiana*, which also occurs scattered in rocky pastures with *Crataegus crus-galli*. Here *Aquilegia cabadensis* is typically found on the ledges, and where there is less soil, *Campitosorus rhizophyllus* and *Pellaea atropurpurea*. Social groups of *Oxalis stricta* *Plantago virginica* and *Antennaria canadensis* grow in dry pastures among grasses and sedges.

Proceeding to Chester loam we find *Ulmus americana* is still present but sparse, and *Fraxinus americana* is now dominant, succeeding *Castanea dentata*, the blighted chestnut. *Prunus Mahaleb* and *P. pennsylvanicum* are frequent; *Quercus alba*, *Q. rubra*, *Q. velutina* and *Liriodendron* are found much as on the preceding loam, while species of *Carya* are better represented, especially by *C. ovata*. But all of these species grow in rather close formation with abundant undergrowth, a second story, of *Cornus florida* and smaller shrubs of *Corylus americana*, *Benzoin aestivale* and *Viburnum molle*. *Vitis cordifolia* does not form as luxuriant a growth while *V. labrusca* is more frequent.

More leaf-mold is found with occasional mycorhiza, and moisture is better retained. There are more species of herbs, these forming a close ground cover of *Smilacina racemosa*, *Sanguinaria canadensis*, *Asarum canadense*, *Podophyllum peltatum* and others, later being succeeded by families of *Osmunda Claytoniana*, *Collinsonia canadensis* and *Aster divaricatus*. *Stellaria media* is replaced by *Galium aparine*.

Moisture is usually well retained by Manor soil of woods and there are many species, but because of greater sterility these do not have as luxuriant a growth; the average rate of growth seems to be less.

Castanea dentata was once dominant but has been replaced by *Carya glabra*, *Liriodendron tulipifera* and *Quercus alba*. The last is most noticeable but not

numerically greater; *Q. rubra* and *Q. velutina* are less frequent while we see *Q. prinus* entering as on the less acid side of its range. *Fagus grandifolia* comes next while *Prunus Mahaleb* is apparently on the acid side of its range. As on Chester soil, *Cornus florida* forms the chief part of the second story, with *Acer rubrum*, *Sassafras variifolium*, *Nyssa sylvatica* and *Prunus virginiana* sub-dominant. Facies of the third story are *Benzoin aestivale* and *Viburnum acerifolium*; *Vitis cordifolia* is still less developed. We see now a true fourth story, of *Vaccinium pensylvanicum* *Rhus toxicodendron* and species of *Rubus*. *Smilax rotundifolia* appears as rather a weak growth. There are many herbs as on Chester loam, and there appear ericads, as *Pyrola americana*, *Solidago caesia* and *Aster divaricatus* are typical of the late aestival aspect.

Phases of Manor loam found in ravines resemble more closely Chester loam while on exposed hill-slopes the vegetation is quite different, consisting of sparse and often stunted growth of *Quercus prinus*, *Kalmia latifolia*, *Rhododendron nudiflorum* and other acid-land plants. This phase has not been considered in the study of Manor loam.

There is a resemblance between this acid hill phase of Manor and the hill-side phase of Dekalb loam; the latter also has phases which are more nearly neutral, in ravines, but vegetation does not make the same amount of growth, the formation is more open, and species are fewer. The soil, being sandy with sandy subsoil, does not retain water; an acid leaf-mold is typical, but aeration is usually good. In ravines we find *Quercus alba* and *Acer rubrum* with sparse *Liriodendron* and *Diospyros virginiana*, and considerable shrub-stratum and herbaceous undergrowth. On gentle hillslopes, considered as typical Dekalb, *Q. alba* is still dominant but *Castanea dentata* was once as numerous; *Q. rubra*, *Q. velutina* and *Carya glabra* are sparse. Higher, *Populus grandidentata* and more frequently *Betula lenta* occur. There is no great distinction between second and third stories, *Cornus florida* and *Acer rubrum* tending to form shrub-growths while *Amelanchier canadensis* is a small tree. *Nyssa sylvatica* becomes copious in places. A bush-stratum, chiefly ericaceous, occurs while herbs are sparse in scattered families.

The ericads become more numerous as we ascend, notably *Gaylussacia baccata*, while *Smilax rotundifolia* becomes copious. Above, on the exposed summit of the hill-range, there is an open formation of *Quercus prinus*, a shrub stratum of sparse *Kalmia latifolia* and patches of *Epigaea repens*, of *Polytrichum* or *Leucobryum*. The soil is decidedly more acid than the type; this phase as well as the ravine have not been included in the tabulated results.

From this soil we pass to Conowingo where in the true type bed-rock comes almost to the surface. On this shallow soil, moist in spring, baked in summer, is found *Nostoc* while the rocks are damp, and fruiting *Cladonias*, while later *Ceratium velutinum*, *Arabis lyrata* and *Thalinum teretifolium* bloom. Open spaces may be bare in part but are usually covered with *Andropogon scoparius*, *Paspalum pubescens*, *Phlox sublata* and *Aster depauperatus*. On the barrens *Pinus virginiana* and *Quercus stellata* replace it.

* Conowingo clay has been treated as the type in this paper; it covers a larger area than the barrens. The soil is a light powder when dry, into which water does not penetrate readily; beneath is a stiff clay. Leaves do not decay rapidly and the partly decomposed remains are knit by hyphal strands; mycorrhiza are abundant. Fruiting bodies of species of *Clavaria* and of *Fistulina hepatica* are found while on logs are bracket fungi,—not the Myxomycetes and Gasteromycetes of moisture situations, as of Chester loam and ravines of Manor loam.

Plant growth is slow and species are not numerous. *Quercus alba* is dominant with *Fagus* sub-dominant, the trees never reaching a large size. Other trees as *Acer rubrum* and *Nyssa sylvatica* are slender but not clumped. There is practically no shrub stratum, as we found also in dry phases of Hagerstown loam, but plants representing the fourth story of Manor loam are numerous, being ericaceous. In the acid leaf-mold may be found families of *Mitchellia repens*, orchids (*Cypripedium acaule*) and ericads as *Chimaphila maculata*. This undergrowth is less than two feet high and the woods are open. Quadrat surveys for density of species do not give a true idea of the vegetation for some plants are as numerous as on other loams, but are dwarf in size so that the total weight of vegetation per quadrat may be but a third of that on better soils.

CONCLUSIONS

Soil-acidity is one of the ecological factors in plant growth. It apparently has a different significance for different species, and is possibly never the independently controlling factor. Its exact effect on the plant and the way in which it exerts this effect is still unsettled.

While different soil types, covered by the same (deciduous forest) formation, show different facies, this seems due to a combination of factors, of which available soil moisture is not an inconsiderable one.

SUMMARY

In order to determine the actual soil acidity in a small area throughout the year, with its effect on root distribution and the ecological distribution of wild plants, an intensive study was made of a region about Paoli, Pennsylvania, in Chester County, including five soil types. Borings were made with a soil auger and the samples thus obtained were tested colorimetrically.

Tests showed that the acidity increases to a depth of about 15 cm. after which it decreases, the increase being greatest in the most sterile soils. Soil acidity seems to be correlated with the productiveness of the soil. Monthly tests reveal that there are slight variations from time to time in the soil acidity of a given spot, and that plants growing here cannot be sensitive to small variations in the acidity. Excessive drying, as in drought, was usually accompanied by an increase in acidity, while heavy rains lowered it; acidity was also

increased during freezing. Decay and leaching does not offer a sufficient explanation for the type of curve found, for the same type was found in agricultural soils.

Absorbing roots were found chiefly in the least acid portions of soil, associated with fungi as mycorhiza in the top 15 cm. of the more acid soils, the mycorhiza becoming less abundant in the more nearly alkaline.

Descriptions of consociies of the soil types are given, indicating a correspondence between not only the facies, but the whole flora, and its habitat.

REFERENCES

- (1) ARRHENIUS, O. 1920 *Oecologische Studien in den Stockholmer Schaeren*, p. 17. Arrhenius, Stockholm.
- (2) ARRHENIUS, O. 1921 The hydrogen-ion concentration of Egyptian soils and the reclamation of alkaline land. *In Cairo Sci. Jour.*, v. 10, p. 1-19.
- (3) BURGESS, P. S. 1922 The hydrogen-ion concentration of soils as affected by drying. *In Science*, n.s., v. 55, p. 647-648.
- (4) CLEMENTS, F. E. 1920 Plant indicators. The relation of plant communities to process and practice. Carnegie Inst. Washington. Pub. 290, p. 375.
- (5) COVILLE, F. V. 1913 Agricultural utilization of acid lands by means of acid-tolerant crops. U. S. Dept. Agr. Bul. 6.
- (6) KELLEY, A. P. 1922 Plant indicators of soil types. *In Soil Sci.*, v. 13, p. 411-423.
- (7) MARSHALL, C. E. 1921 *Microbiology*, p. 345-374. Blakiston, Philadelphia.
- (8) MOORE, G. T. 1912 Microorganisms of the soil. *In Science*, n. s., v. 36, p. 609-615.
- (9) NEMEC, A., AND KAREL, K. 1923 *Étude biochimique des sols forestier*. *In Compt. Rend. Acad. Sci., Paris*, v. 176, p. 260-262.
- (10) SALISBURY, E. J. 1922 Stratification and hydrogen-ion concentration of the soil in relation to leaching and plant succession with especial reference to woodlands. *In Jour. Ecol.*, v. 9, p. 220-240.
- (11) WEAVER, J. E. 1919 The ecological relations of roots. Carnegie Inst. Washington. Pub. 286.
- (12) WHERRY, E. T. 1920 Soil acidity and a field method for its measurement. *In Ecology*, v. 1, p. 160-173.
- (13) WHERRY, E. T. 1920 Observations on the soil acidity of *Ericaceae* and associated plants in the Middle Atlantic States. *In Proc. Acad. Nat. Sci. Phila.*, v. 72, p. 84-113.
- (14) WHERRY, E. T. 1922 Recent work on soil acidity and plant distribution. *In Science*, n.s., v. 55, p. 568-570.
- (15) WILDER, H. J., CAINE, T. A., GEIB, W. J. AND CARTER, W. T., JR. 1906 Soil survey of Chester County, Pennsylvania. U. S. Dept. Agr., Bur. Soils, Advance sheets, field operations, 1905, p. 1-44.

MICROBIOLOGICAL ANALYSIS OF SOIL AS AN INDEX OF SOIL FERTILITY: VI, NITRIFICATION¹

SELMAN A. WAKSMAN

New Jersey Agricultural Experiment Stations

Received for publication May 21, 1923

A number of investigators have observed a definite parallelism between the nitrifying capacity and the crop-producing power of the soil, both by the use of the Remy-Löhnis liquid culture method and the fresh soil (or tumbler method). We need call attention only to a few of the outstanding and some of the more recent contributions to this subject.

Löhnis (23) following the work of Remy obtained definite differences in the nitrifying powers of soils bearing upon crop production. A standard solution to which soil extract has been added was used in these studies. Kellerman and Allen (15) demonstrated in 1911 that a close correlation exists between the nitrifying capacity of soils in arid regions and productivity. The relative nitrifying power of very productive soil was found to be 54; of productive soils, 20-36; and of poor soils only 3-5. Greaves (10) found a nearly quantitative relationship between the number of colonies developing on the plate, milligrams of nitric nitrogen formed and nitrogen fixed in cultivated and virgin soils. A correlation between nitrification and soil productivity has also been found by Gutzeit (12), Vogel (29), Brown (3), Noyes and Conner (24), Lipman, C. B. (19), and others, while a close correlation between a high nitrifying power and high productivity has also been observed by Ashby (2), Stevens and Withers (28), Given (9), and Gainey (7). Burgess (4), using the soil method, reported that nitrification is by far the most accurate biological soil test yet perfected for predicting probable fertility. Fischer (5) stated that nitrification can be used for soil characterization. Fraps (6) pointed out that the nitrification test enables one to trace the effect of cropping upon the nitrogen of the soil; ammonia determinations, however, give no increased correlation over the determinations of nitric nitrogen alone. Numerous other observations have been made as to the value of nitrification studies in characterizing soil fertility, including also forest soils. This biological phenomenon can also be used to indicate a distinction between available and unavailable nitrogen, as pointed out by Lipman and Burgess (20, 21).

In some cases, however, the correlation is questioned. Allen and Bonazzi (1), for example, found that the nitrifying capacity of a soil may or may not correlate with its crop producing power, while continuous cropping, especially without fertilization, reduces the nitrifying power of soils. Gerretsen (8) questioned the importance of nitrification as an index of soil fertility, although the two were found to run parallel. The lack of correlation between soil productivity and its nitrifying capacity as reported in some cases may be due merely to the faulty method used in determining the latter.

As pointed out in the previous paper of this series (32), when ammonium sulfate is used for the study of nitrification in soil, especially in the case of acid and poorly buffered soils, the hydrogen-ion concentration resulting from the oxidation of the ammonium salt used in the

¹ Paper No. 133 of the Journal Series, New Jersey Agricultural Experiment Stations, Department of Soil Chemistry and Bacteriology.

test soon reaches a maximum for the growth and activities of the nitrifying bacteria. Accordingly, when we compare two soils of nearly equal productivity, of which one has received an application of lime while the other has not, the former will show a much higher nitrifying capacity. This difference is due merely to the inadequacy of the common method in which an excess of the ammonium salt is used. This was recognized by Allen and Bonazzi (1), who stated that the customary methods used in studying nitrification are so fraught with errors that we can never hope to solve by them the complex problems encountered. Stevens and Withers (27), for example, reported that 71 per cent of the North Carolina soils do not nitrify. Kellerman and Robinson (17), however, observed a definite correlation between poor nitrification, acid reaction of soil and lack of nodule formation.

When dried blood or other highly concentrated organic nitrogenous substances are used in the nitrification tests, results may again be faulty, particularly in alkaline, poorly buffered soil, due to the large amount of dried blood usually used in the test. The excess of ammonia formed, from the decomposition of the dried blood, in the absence of sufficient buffer or acid substances to neutralize it, will injure greatly the activities of the nitrifying bacteria. Lipman and Burgess (20), for example, found that semi-arid humus-poor soils do not nitrify dried blood which might lead to the conclusion that the use of dried blood as a fertilizer on those soils is inadvisable. Kelley (18) soon pointed out that when, instead of 1 per cent of dried blood, this material is added in low concentrations, the same soil will nitrify it very actively. Kelley concluded, therefore, that results obtained with the use of such high concentrations as 1 and 2 per cent of dried blood or 0.3 and 0.6 per cent of ammonium sulfate, are not a reliable basis for practical conclusions.

Because of the lack of the proper method for studying nitrification, Kelley (18) stated that, "the practical aspects of nitrification studies have become extremely empirical."

The influence of reaction upon nitrification can, therefore, account for a good many results, in which a lack of correlation between nitrification and soil productivity has been recorded. We need but refer here to the work of Wohltmann and associates (34), who found that while the addition of CaO to an acid soil increased its nitrifying capacity (using the soluton method) from 14.1 to 84.7 per cent, the application of manure increased nitrification from 14.1 to 36.1 per cent; $(\text{NH}_4)_2\text{SO}_4$ to 23.0 per cent; NaNO_3 , to 31.9 per cent, K_2O and P_2O_5 , to 17.8 per cent. The lack of parallelism between nitrification and crop productivity of soils having different reactions particularly when ammonium sulfate is used as the source of nitrogen, is due to the fact that the amount of nitrate formed, under laboratory conditions, is governed by the initial and final soil reactions, as well as presence of bases and buffer content, rather than by the actual nitrifying capacity of the soils, as pointed out elsewhere (32). It is only when the reactions of two or more soils are alike, that nitrification can be compared with soil productivity. Even then we should consider the buffer and base content of the soils.

Stevens and Withers (28) have shown that legumes and stable manure increase the nitrifying efficiency of soils. The favorable influence of manure on nitrification has also been pointed out by Heinze (14), Greaves and Carter (11) and various other investigators. According to Guistiniani (13), nitrification of ammonium sulfate is proportional to moisture content of the soil. Cultivation of soil and addition of organic matter stimulate nitrate formation in soil, as shown by Noyes and associates (25).

Just as in the study of the variability of soil as far as the distribution of numbers of micro-organisms are concerned, the variability of the nitrifying capacity of the soil should be considered. Waynick (33) found that the variability of the nitrate content of field samples of soil taken even from an apparently uniform and limited area is high and is of great importance in the estimation of the reliability of any series of results. The variability is still further increased when the samples are treated by the tumbler method for nitrification studies. A single sample was found to be of little value and even a limited number of samples (10 to 16) are subject to wide variations and can give results having only a low degree of accuracy. A composite sample may be considered of value only after the probable error has been determined by the use of a large number of individual samples. Prince (26) compared, at this

laboratory, the variability of the nitrate content and nitrifying capacity of the soil in plots 5A, 7A and 9A, which are described below. Taking twenty-five samples from each plot, he found the coefficient of variability to range between 13 and 42 per cent and the probable error of the mean from 2 to 5 per cent. He found a definite correlation between the crop yields of the three plots with the number of microorganisms and the nitrifying power of the soil.

EXPERIMENTAL

Methods

The following methods were used for the study of nitrification in an attempt to learn whether there is a definite correlation between the nitrifying power of a soil and its crop producing power.

1. Nitrification in pure sand, 100 gm. of pure washed sand and 210 mgm. of CaCO_3 were placed in 250 cc. Erlenmeyer flasks and moistened with 10 cc. of distilled water or with a solution containing 1 gm. K_2HPO_4 , 0.5 gm. MgSO_4 and 0.01 gm. FeSO_4 in 1000 cc. of distilled water; the flasks were plugged with cotton and sterilized in the autoclave, at 15 lbs. for 1-2 hours. To each flask were added 5 cc. of a sterile solution of ammonium sulfate equivalent to 30 mgm. of nitrogen. For the inoculation 10 gm. of soil per flask was used. The flasks are then incubated at 27-28°C. for 30 days. This method, just as in the case of the solution methods, is more qualitative than quantitative in nature. The results are apt to be erratic and vary greatly. They are, therefore, more indicative of the activity of the nitrifying flora of the soil than of the nitrate-forming capacity of a given soil itself.

2. Nitrification of soil's own nitrogen. 100-gm. portions of fresh, sieved soil were placed in tumblers, covered with petri dishes and kept at an optimum moisture in the incubator for 30 days.

3. Thirty milligrams of nitrogen as ammonium sulfate per 100 gm. of soil, and treated as 2.

4. Thirty milligrams of nitrogen as ammonium sulfate and 210 mgm. of CaCO_3 per 100 gm. of soil. The carbonate is first well mixed with the soil, then the ammonium salt is added. A 21-to 24-day incubation period is sufficient for this test.

5. Dried blood (0.25 gm.) was well mixed in with 100 gm. of fresh sieved soil, kept at optimum moisture in the incubator for 15 days; then the ammonia and nitrate are determined.

As pointed out in the previous paper (32), each one of these methods contributes information necessary for a complete picture of the nitrifying capacity of the soil. This is particularly true of method 4, where the nitrifying capacity of ammonium sulfate is studied in the presence of sufficient CaCO_3 to neutralize all the acid formed from the complete nitrification of the ammonium salt.

The nitrates were determined by the phenol-disulfonic acid method. Fifty grams of soil were shaken with 200 cc. of water for about 10-15 minutes in 500-cc. Erlenmeyer flasks, in the presence of a small amount of CaO and filtered through paper. Twenty cubic centimeters of the filtrate were evaporated and treated as usual. The data for nitrification are always given on the basis of milligrams of nitrate nitrogen in 100 gm. of soil.

Soils

The same series of nitrogen plots used in the previous studies (30, 31) were also used for the study of nitrification in the following experiments. The soils were sampled with a borer to a depth of 6.5 inches; 15-25 samples were taken from each plot. The samples were well mixed and sieved through a 3 or 5 mm. sieve. Approximately 60 per cent of the moisture-holding capacity of the soil was used since this was considered an optimum moisture content.

Variability of nitrate content of the soils studied

Plot 9A receiving minerals and 320 pounds of NaNO₃ per acre was sampled for the study of nitrate distribution. Fifty-one samples were taken from this plot which is 1/20 of an acre in size. The samples were taken in rows, about equal distance both ways, the outside rows being about three feet from margin of plot. The results are reported in table 1.

TABLE 1
Residual nitrate in soil 9A

SAMPLE NUMBER	NITRATE NITROGEN	DEVIATION FROM MEAN \pm	SAMPLE NUMBER	NITRATE NITROGEN	DEVIATION FROM MEAN \pm
	mgm.	mgm.		mgm.	mgm.
1	0.65	0.08	29	1.07	0.34
2	1.10	0.37	30	0.21	0.52
3	1.56	0.83	31	0.32	0.41
4	0.92	0.19	32	1.25	0.52
5	0.96	0.23	33	0.33	0.40
6	0.63	0.10	34	1.54	0.81
7	0.86	0.13	35	0.32	0.41
8	0.58	0.15	36	0.27	0.46
9	1.10	0.37	37	0.38	0.35
10	0.65	0.08	38	0.42	0.31
11	1.25	0.52	39	0.45	0.28
12	1.05	0.32	40	0.47	0.26
13	0.42	0.31	41	1.42	0.69
14	0.51	0.22	42	0.86	0.13
15	0.48	0.25	43	0.53	0.20
16	0.60	0.13	44	1.11	0.38
17	0.83	0.10	45	0.35	0.38
18	0.43	0.30	46	0.39	0.34
19	0.46	0.27	47	1.26	0.53
20	0.95	0.22	48	0.75	0.02
21	0.96	0.23	49	0.28	0.45
22	1.28	0.55	50	0.58	0.15
23	0.49	0.24	51	0.17	0.56
24	0.65	0.08			
25	1.02	0.29		Mean	0.73 \pm 0.03
26	0.44	0.29			$\sigma = 0.35 \pm 0.02$
27	0.41	0.32			C.V. = 47.9 \pm 2.9%
28	1.08	0.35			E _m = 4.5%

As the average of 61 determinations, the soil in the nitrate-treated plot contains 0.73 mgm. of nitrate nitrogen in 100 gm. of soil or approximately 14.6 pounds per acre. The range is, however, between 1.6 and 30.8 pounds. It is interesting to note that Waynick (33) found by determining the nitrate nitrogen in 100 samples of a California soil 2.70 ± 0.05 mgm. in the surface soil and 0.70 ± 0.03 mgm. in the subsoil, with an average error for the latter of 4.3 per cent. In other words, the amount and variability of the nitrate nitrogen in the plot examined is similar to that found by Waynick in the California sub-soil.

To compare the influence of the period of incubation upon nitrate accumulation in the variously treated soils from organic and inorganic sources of nitrogen, a series of tumblers were prepared using dried blood and ammonium sulfate. At definite intervals, two or three tumblers were taken out for the determination of nitrate, reaction and, in the case of the dried blood, of ammonia. The latter was done with the idea of demonstrating whether the formation of ammonia in the decomposition of the proteins ever becomes a limiting factor to nitrification. A large quantity of the protein source (1 per cent) was used in this experiment so as to have an excess of ammonia present.

As seen in table 2, ammonia formation from dried blood never becomes a limiting factor in the process of nitrification, at least for the soils used in these experiments. Nitrate accumulation depends, however, on the buffer content and the initial reaction of the soil. The results obtained after 15 and after 41 days are distinctly different for the variously treated soils. While the course of nitrate formation was uninterrupted in the case of the manured soils (5A and 5B) and also in the case of the most acid plot (11A), it rapidly came to a stop in the case of the limed and poorly buffered soils. The explanation to that is found in the columns which give the hydrogen-ion concentrations of the soil i.e., the excess of ammonia brought about a rapid increase in the alkalinity of the soil, which completely depressed nitrate formation. It is interesting to note that out of a total of 125 mgm. of nitrogen added to the soil (the dried blood containing 12.5 per cent nitrogen), nearly 121 mgm. were converted into ammonia and nitrate by the most fertile soil (5A); this, of course, includes about 10 mgm. that would have accumulated otherwise in the soil itself.

The results obtained with ammonium sulfate again show that the limiting factor is not the biological flora of the soil, but the initial and final reactions as well as the buffer content of the soil. These phenomena have been considered in detail in the previous paper and need not be dwelt upon here longer.

The soils were sampled five times during the year 1922-1923 and the nitrifying capacity tested by the different methods. The results on nitrate accumulation are given in tables 3-7, while the bacterial numbers for the corresponding dates are reported in table 8. A summary of the treatment, crop yields, bacterial numbers and nitrifying capacity of the various plots are given in table 9.

The results indicate that there is a definite correlation between the nitrifying capacity of a soil and crop productivity, especially in soils not modified by the application of lime. The nitrifying capacity of the soil depends on the physical, chemical and biological conditions of the soil, the most important of the physical and chemical factors being the buffering properties of the soil, hydrogen-ion concentration, presence of lime and perhaps of soluble phosphates and other minerals. The number and efficiency of the organisms oxidizing ammonia to nitrates, as well as the amount of nitrate removed by soil fungi and bacteria, account for the biological efficiency of a soil to accumulate

TABLE
Course of nitrate formation from dried blood and ammonium sulfate in variously treated soils, May 22, 1922

ELUT NUMBER	DRIED BLOOD* (1 PER CENT)						AMMONIUM SULFATE (30 MG.M. OF N IN 100 GM. OF SOIL)						Reaction after							
	NO ₂ -N in 100 gm. soil			Reaction after			NO ₂ -N in 100 gm. soil after:			Reaction after			NO ₂ -N in 100 gm. soil after:			Reaction after				
	7 days mg.m.	41 days mg.m.	3 days mg.m.	7 days mg.m.	15 days mg.m.	27 days mg.m.	0 days mg.m.	3 days mg.m.	7 days mg.m.	15 days mg.m.	27 days mg.m.	0 days mg.m.	3 days mg.m.	7 days mg.m.	15 days mg.m.	27 days mg.m.	0 days mg.m.	3 days mg.m.	7 days mg.m.	
5 A	45.2	64.9	5.6	6.0	13.8	42.2	56.0	5.4	6.2	7.1	7.4	5.8	0.7	1.8	4.3	5.9	5.4	5.2	5.0	4.7
7 A	38.1	72.8	3.4	2.7	3.1	4.8	4.4	6.2	7.0	7.6	8.1	0.13	0.2	0.56	0.40	4.8	...	4.4	4.4	4.4
9 A	34.0	76.2	5.1	4.1	6.7	7.6	5.8	6.4	7.3	7.8	8.2	0.7	2.2	4.8	4.4	5.4	...	4.6	4.6	4.6
11 A	44.2	87.8	3.1	2.1	3.5	5.0	15.2	4.6	6.6	7.0	7.6	7.9	0.3	0.4	0.5	0.4	4.4	...	4.2	4.2
19 A	39.3	82.6	4.9	3.0	3.8	8.8	4.6	5.4	6.4	7.2	7.8	8.0	0.2	0.5	1.6	1.7	5.2	4.9	4.4	4.4
5 B	42.0	45.5	9.1	10.2	17.0	43.2	52.0	6.4	7.6	8.0	7.5	6.8	2.4	5.6	12.4	16.1	5.6	5.2	4.6	4.4
7 B	40.1	49.8	5.0	3.4	4.4	5.4	4.6	6.2	7.8	9.0	8.8	8.4	0.5	2.5	7.2	9.4	5.3	...	4.6	4.4
11 B	47.5	59.5	3.4	3.2	3.4	4.9	5.2	5.7	7.1	8.5	8.6	8.6	0.4	0.9	3.8	4.9	5.4	...	4.6	4.4

* By nitrates, we must understand all substances giving the characteristic reaction with phenol-disulfonic acid. The dried blood, for example, used in our studies was found to contain about 3 mgm. of nitrate-nitrogen in 1 gm. of dried blood, as determined by the phenol-disulfonic acid method.

TABLE 3
Nitrification of ammonium sulfate in sand plus CaCO₃

PLOT NUMBER	JULY 10, 1922	DEC. 6, 1922	APR. 3, 1923	AVERAGE
	mgm.	mgm.	mgm.	mgm.
5 A	2.80	1.35	0.72	1.62
7 A	0.21	0.14	0.09	0.14
9 A	0.68	0.20	0.44
11 A	0.44	0.40	0.12	0.32
19 A	0.22	0.15	0.19
5 B	4.30	0.65	2.48
7 B	0.94	0.21	0.51	0.55
11 B	2.20	1.30	0.26	1.25
19 B	0.56	0.30	0.43

TABLE 4
Nitrification of soil's own nitrogen

PLOT NUMBER	JULY 10, 1922	AUG. 17, 1922	DEC. 6, 1922	APR. 3, 1923	AVERAGE
	mgm.	mgm.	mgm.	mgm.	mgm.
5 A	2.50	1.24	0.98	2.30	1.76
7 A	0.38	0.48	0.52	0.70	0.52
9 A	0.84	0.74	1.25	0.94
11 A	0.84	0.52	0.78	1.05	0.80
19 A	0.76	0.74	1.05	0.85
5 B	0.72	1.90	1.31
7 B	0.60	0.58	0.26	0.75	0.55
11 B	0.94	0.22	0.58	0.90	0.66
19 B	0.96	0.48	1.30	0.91

TABLE 5
*Nitrification of ammonium sulfate in soil**

PLOT NUMBER	MAY 22, 1922*	JULY 10, 1922*	AUG. 17, 1922	DEC. 6, 1922	APR. 3, 1923	AVERAGE
	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
5 A	4.30	5.20	3.90	3.90	3.80	4.22
7 A	0.56	0.38	0.37	0.41	0.50	0.44
9 A	4.80	4.90	3.10	3.30	3.60	3.90
11 A	0.50	0.76	0.49	0.53	0.30	0.52
19 A	1.60	1.72	0.94	0.82	1.20	1.26
5 B	12.40	11.60	10.70	7.80	7.20	9.94
7 B	7.20	6.20	8.60	4.10	4.10	6.04
11 B	3.80	3.80	6.10	2.90	2.90	3.90
19 B	10.40	8.90	9.20	5.00	5.20	7.74

* Incubation period for samples taken May 22 and July 10 was 30 days; for the rest, only 25 days.

TABLE 6
Nitrification of ammonium sulfate, in presence of a theoretical amount of CaCO₃

PLOT NUMBER	JULY 10, 1922*	AUG. 17, 1922	AUG. 30, 1922	DEC. 6, 1922	APR. 3, 1923	AVERAGE
	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
5 A	24.40	33.40	30.40	17.40	23.20	25.76
7 A	7.60	7.10	5.20	4.30	6.80	6.20
9 A	22.10	23.20	19.60	13.70	19.60	19.64
11 A	3.10	11.40	4.40	6.90	7.80	6.72
19 A	7.90	11.80	6.60	6.50	9.90	8.54
5 B	30.90	30.80	29.60	23.30	29.40	28.80
7 B	16.95	26.10	25.80	15.20	20.20	20.85
11 B	26.60	32.20	22.60	19.30	25.30	25.20
19 B	24.20	28.60	29.60	19.60	26.30	25.66

* 50 mgm. of nitrogen used in this case.

TABLE 7
Nitrification of dried blood (0.25%) in the soil

PLOT NUMBER	JULY 10, 1922*	AUG. 17, 1922	AUG. 30, 1922	DEC. 6, 1922	APR. 3, 1923	AVERAGE
	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
5 A	24.40	10.20	7.60	6.40	6.10	10.94
7 A	7.20	2.40	2.00	2.30	1.60	3.10
9 A	17.20	6.00	7.40	5.30	5.10	8.20
11 A	5.00	2.20	1.20	2.40	1.50	2.46
19 A	8.60	2.80	2.40	3.10	2.50	3.88
5 B	25.30	19.20	15.00	15.10	14.60	17.84
7 B	18.30	13.60	8.40	9.40	7.10	11.36
11 B	21.20	15.40	11.60	10.60	5.00	12.76
19 B	20.10	17.00	10.80	8.90	10.70	13.50

* Incubation period 25 days for July 10 sampling and 13-15 days for the other dates.

TABLE 8
Numbers of microorganisms in the soil (thousands per gram)

PLOT NUMBER	JULY 10, 1922	AUG. 17, 1922	AUG. 30, 1922	DEC. 6, 1922	APR. 3, 1923	AVERAGE
5 A	16,660	8,890	14,500	15,540	14,000	13,920
7 A	6,180	5,430	6,800	3,000	5,300	5,342
9 A*	10,600	13,250	8,800	11,700	11,088
11 A	5,540	7,600	5,100	5,100	4,400	5,548
19 A	6,770	9,440	4,800	7,900	7,228
5 B	13,560	8,410	11,600	10,800	14,600	11,794
7 B	8,600	8,110	7,200	6,500	9,900	8,062
11 B	10,700	9,260	8,350	6,600	9,500	8,882
19 B	9,500	9,600	7,700	12,000	9,700

* Attention should be called here to an unpardonable error that has crept into the graph of the third paper of this series (30) where 9B should read 9A.

TABLE 9
Chemical and biological condition of soil and crop productivity

PLOT NUMBER	NITROGEN CONTENT*	CARBON CONTENT*	NITROGEN APPLIED PER ACRE IN 14 YEARS	NITROGEN RECOVERED IN CROP IN 14 YEARS	CROP YIELD PER ACRE	RE-ACTION	BACTERIAL NUMBERS		NITRIFYING CAPACITY			
							per cent	lbs.	lbs.	per H.	millions	NO ₂ -N per 100 gm. soil
5 A	0.1463	1.73	2519	690	69,500	5600	5.5	13.9	262	8	86	450 Minerals§ and 16 tons of cow manure
7 A	0.0826	0.96	0	164	15,464	328	5.0	5.3	100	2	08	100 No fertilizer
9 A	0.0994	1.17	693	557	57,968	4480	5.8	11.1	210	6	62	318 Minerals and 320 lbs. NaNO ₃
11 A	0.1064	1.23	693	497	41,754	180†	4.6	5.5	104	2.16	104 Minerals and (NH ₄) ₂ SO ₄ equivalent to 320 lbs. NaNO ₃	
19 A	0.1008	1.13	0	294	29,926	660	5.4	7.2	136	2	82	135 Minerals only
5 B	0.1428	1.74	2519	606	59,754	4720	6.4	11.8	223	12	07	580 Minerals, manure, and lime
7 B	0.0868	1.18	0	312	30,160	960	6.3	8.0	151	7	87	378 Lime only
11 B	0.0952	1.10	693	635	61,906	4680	5.8	8.9	168	8.75	440 Minerals, (NH ₄) ₂ SO ₄ and lime	
19 B	0.0924	1.18	0	341	35,930	2400	6.4	8.7	183	9.65	464 Minerals and lime	

* The total carbon and nitrogen in this summary differ from those given in a previous paper, the former being determined this year in this laboratory, while the latter was taken from the paper of Lipman and Blair (22).

† Also 1100 pounds *Rizomex acetosella*.

‡ Average of the five different tests.

§ Minerals = 640 pounds acid phosphate and 320 pounds of potassium chloride per acre.

|| B plots received per acre 1 ton of lime in 1908; 2 tons, in 1913; and 2 tons, in 1918.

nitrates. It is important to note that here again, even more than in the case of numbers, the addition of lime to the soil brought about a greater stimulus to the nitrifying efficiency of the soil than in crop productivity. This is due chiefly to our methods of studying nitrification, whereby amounts of nitrogen sources are added to the soil much in excess of what would be used under field conditions. Under these artificial conditions, where acids are formed from the oxidation of the ammonium salt by organisms which are rather sensitive to an excess of acid, it is but natural to expect that the addition of lime to the soil will favor the process of nitrification in the laboratory, independent of

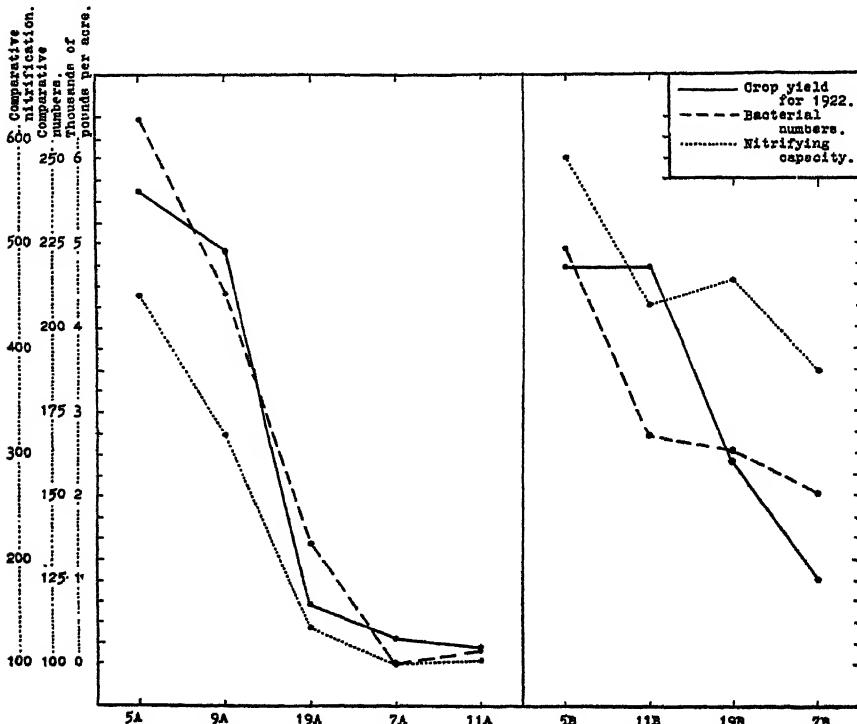


FIG. 1. INFLUENCE OF SOIL FERTILIZATION UPON CROP YIELD, NUMBERS OF MICROORGANISMS DEVELOPING ON THE PLATE AND NITRIFYING CAPACITY OF THE SOIL

its actual effects under field conditions. It is sufficient to inspect table 4 to find that no more nitrate will accumulate in the soil, without any addition of an excess amount of nitrogen, in the limed than in the unlimed soils. We can expect a more accurate correlation and the elimination of the disturbing influence of liming of soil only after we have developed our methods to an extent as to have laboratory conditions absolutely comparable with phenomena taking place in the field.

The graphs in figure 1 show conclusively that there is a correlation between the crop productivity of the soil on the one hand and numbers of microorgan-

isms and nitrifying capacity of the soil on the other, allowing for the disturbing influence of liming of an acid soil. The fertility of a soil is affected not only by its biological phenomena but also by its physical and chemical conditions, especially by the amount of fertilizing elements present in the soil or added previous to, or during the process of growth, as well as by the kind of crop grown. We cannot expect, therefore, that the results of a biological study of soil, especially if not all activities are concerned and properly interpreted, should give an exact mathematical interpretation of the productive capacity of the soil. It is sufficient to point out the parallelism. This combined with our knowledge of the physical and chemical nature of the soil can explain the productivity of the soil.

SUMMARY

In the study of soil microbiological methods as a possible means of measuring the present and future crop-producing power of soils, certain relations and tendencies are clearly indicated. Soil microbiological research has not yet gone far enough to justify our using any soil microbiological factor as an index of soil productivity. Nevertheless, the author feels justified in pointing out that the data submitted in the present paper together with those published previously bring out certain correlations, which may help in time to place in our hands quantitative as well as qualitative methods for measuring the productive power of soils.

The results presented in this paper on the nitrifying power of the soil indicate that nitrification studies can yield information for the differentiation of soil fertility just as well as the study of numbers of microorganisms in the soil. Liming of the soil stimulates the nitrifying capacity of the soil and affects, therefore, the parallelism between the results obtained in the laboratory from the study of nitrification and crop yields. However, since soil fertility is affected, aside from the biological activities of the soil, also by its physical and chemical conditions, the results should not be expected to be a mathematical function of crop productivity of a given soil.

It is necessary to add here a further word of caution, so as to prevent any misunderstandings that might have arisen from the studies reported in these papers. The results of the investigations thus far reported indicate that a study of numbers of microorganisms in the soil and of nitrification yield results which can be used as indices of soil fertility; it is questionable whether ammonia formation in either soil or solution can be used for that purpose. It is important to keep in mind that these studies have been carried out with one soil type (Sassafras gravelly loam), slightly acid in reaction (uncultivated, about pH = 6.0 to 6.2), divided into a group of plots which have been fertilized alike for a number of years. The differences thus established are due to differences in treatment. It remains to be seen whether the same results will be obtained when various soil types are employed.

The writer is indebted to Mr. R. L. Starkey for aid in taking the samples; to Miss C. Wark for assistance in the laboratory determinations; to Dr. J. G. Lipman and Prof. A. W. Blair for permission to use the soil plots and data on crop yields; and to Dr. J. Lipman for reading the manuscript.

REFERENCES

- (1) ALLEN, E. R., AND BONAZZI, A. 1915 On nitrification. *Ohio Agr. Exp. Sta. Tech. Bul.* 7.
- (2) ASHBY, S. F. 1904 The comparative nitrifying power of soils. *In Jour. Chem. Soc. (London)*, v. 85, p. 1158-1170.
- (3) BROWN, P. E. 1916 Relations between bacterial activities in soils and their crop producing power. *In Jour. Agr. Res.*, v. 5, p. 855-869.
- (4) BURGESS, P. S. 1918 Can we predict probable fertility from soil biological data? *In Soil Sci.*, v. 6, p. 449-462.
- (5) FISCHER, H. 1911 Versuche über Stickstoffumsetzung in verschiedenen Boden. *In Landw. Jahrb.*, v. 41, p. 755-822.
- (6) FRAPS, J. S. 1921 Relation of soil nitrogen, nitrification and ammonification to pot experiments. *Texas Agr. Exp. Sta. Bul.* 283.
- (7) GAINY, P. L. 1917 The significance of nitrification as a factor in soil fertility. *In Soil Sci.*, v. 3, p. 399-416.
- (8) GERRETSEN, F. C. 1921 Een onderzoek naar de nitrificatie en denitrificatie in tropische gronden. *In Arch. Suikerind. Nederlandsch. Indie.*, v. 29, p. 1397-1530.
- (9) GIVEN, G. C. 1913 Bacteriology of the general fertilizer plots. IV. Nitrification. *In Penn. Agr. Exp. Sta. Ann. Rpt.* 1912-13, p. 204-206.
- (10) GREAVES, J. E. 1913 A study of the bacterial activities of virgin and cultivated soils. *In Centrbl. Bakt. (etc.), Abt. 2*, v. 41, p. 444-459.
- (11) GREAVES, J. E., AND CARTER, E. G. 1916 Influence of barnyard manure and water upon the bacterial activities of the soil. *In Jour. Agr. Res.*, v. 6, p. 889-926.
- (12) GUTZEIT, E. 1906 Einwirkung des Hederichs auf die Nitrifikation der Ackererde. *In Centrbl. Bakt. (etc.), Abt. 2*, v. 16, p. 358-381.
- (13) GUISTINIANI, F. 1901 L'humidité des terres et la denitrification. *In Ann. Agron.*, v. 27, pl. 262-285.
- (14) HEINZE, B. 1910 Über die Salpeterbildung im Boden. *In Landw. Mitt. Sachsen* 1909, p. 5-7; *Ref. in Centrbl. Bakt. (etc.), Abt. 2*, v. 26, p. 683.
- (15) KELLERMAN, K. F., AND ALLEN, E. R. 1911 Bacteriological studies of the soil of the Truckee-Carson irrigation project. *U. S. Dept. Agr. Bur. Plant Indus. Bul.* 211, p. 1-33.
- (16) KELLERMAN, K. F., ALLEN, E. R., AND McBETH, I. G. 1910 Nitrification in soils. *Abs. in Science*, n.s., v. 31, p. 280.
- (17) KELLERMAN, K. F., AND ROBINSON, T. R. 1909 Nitrifying bacteria in North Carolina soils. *In Science*, n.s., v. 30, p. 413-414.
- (18) KELLEY, W. P. 1916 Nitrification in semi-arid soils. *In Jour. Agr. Res.*, v. 7, p. 417-438.
- (19) LIPMAN, C. B. 1914 The nitrifying power of soils as indices to their fertility. *In Proc. Soc. Prom. Agr. Sci. 35th Ann. Meeting*, p. 33-39; *Cal. Bul.* 260, p. 107-127.
- (20) LIPMAN, C. B., AND BURGESS, P. S. 1915 The determination of availability of nitrogenous fertilizers in various California soil types by their nitrifiability. *Cal. Agr. Exp. Sta. Bul.* 260, 107-127.
- (21) LIPMAN, C. B., AND BURGESS, P. S. 1917 Ammonifiability versus nitrifiability as a test for the relative availability of nitrogenous fertilizers. *In Soil Sci.*, v. 3, p. 63-75.

- (22) LIPMAN, J. G., AND BLAIR, A. W. 1920 Field experiments on the availability of nitrogenous fertilizers, 1908-1917. *In* Soil Sci., v. 9, p. 371-392.
- (23) LÖHNIS, F. 1905 Untersuchungen über den Verlauf der Stickstoffumsetzungen in der Ackererde. *In* Mitt. Landw. Inst. Univ. Leipzig, v. 7, p. 1-103.
- (24) NOYES, H. A., AND CONNER, S. D. 1919 Nitrates, nitrification, and bacterial contents of five typical acid soils as affected by lime, fertilizer, crop, and moisture. *In* Jour. Agr. Res., v. 16, p. 27-42.
- (25) NOYES, H. A., MARTOLF, J. H., AND KING, H. T. 1922 Cultivation and nitrogen fertilization. *In* Jour. Indus. Engin. Chem., v. 14, p. 299-302.
- (26) PRINCE, A. L. 1923 Variability of nitrates and total nitrogen in soils. *In* Soil Sci., v. 15, p. 395-405.
- (27) STEVENS, F. L., AND WITHERS, W. A. 1909 Concerning the existence of non-nitrifying soils. *In* Science, v. 29, p. 506-508.
- (28) STEVENS, F. L., AND WITHERS, W. A. 1912 Studies in soil bacteriology: V. The nitrifying and ammonifying powers of North Carolina soils. *In* Centrbl. Bakt. (etc.), Abt. 2, v. 34, p. 187-203.
- (29) VOGEL, J. 1910 Beiträge zur Methodik der bakteriologischen Bodenuntersuchung. *In* Centrbl. Bakt. (etc.), Abt. 2, v. 27, p. 593-605; also *in* Fühling's landw. Ztg., v. 59, p. 626-636.
- (30) WAKSMAN, S. A. 1922 Microbiological analysis of soil as an index of soil fertility. III. Influence of fertilization upon numbers of microorganisms in the soil. *In* Soil Sci., v. 14, p. 321-346.
- (31) WAKSMAN, S. A. 1923 Microbiological analysis of soil as an index of soil fertility. IV. Ammonia accumulation (Ammonification). *In* Soil Sci., v. 15, p. 49-65.
- (32) WAKSMAN, S. A. 1923 Microbiological analysis of soil as an index of soil fertility. V. Methods for the study of nitrification. *In* Soil Sci., v. 15, p. 241-261.
- (33) WAYNICK, D. D. 1918 Variability in soils and its significance to past and future soil investigations. I. A statistical study of nitrification in soils. Univ. Cal. Pub. Agr. Sci., v. 3, p. 243-270.
- (34) WOELTMANN, F., FISCHER, H., AND SCHNEIDER, PH. 1904 Bodenbakteriologische und bodenchemische Studien aus dem Versuchsfelde. *In* Jour. Landw., Bd. 52, p. 97-126.

INFLUENCE OF SOIL MOISTURE AND ACIDITY ON THE DEVELOPMENT OF POTATO SCAB¹

WM. H. MARTIN

New Jersey Agricultural Experiment Stations

Received for publication May 24, 1923

In a recent paper Sanford (1) indicates that soil reaction may not be the most important factor in influencing the development of common scab of potatoes. He shows that with an increase in soil moisture content there was a decrease in the amount of infection on the tubers and as a result of hydrogen-ion determinations made of the soils of various moisture content, he found that the dry soils were slightly more acid than the moist soils and concludes that moisture and not acidity was the controlling factor. The differences in the pH values of the dry and moist soils were very slight, however, and in every case the values indicated were within the limiting range for the best development of *Actinomyces scabies*.

As the result of a series of potato scab control and infection studies conducted during the past three years at the New Jersey Agricultural Experiment Stations, considerable data has been accumulated on the relation of the scab organism to soil conditions. The weather conditions, especially rainfall, have been widely different in these three years. In 1920 the rainfall was well above the average and in 1922 slightly above the average, while in 1921 it was below average. In 1920 the mean rainfall for the state for the months of April to September inclusive, was 29.21 inches, for the same months in 1921 and 1922, 21.26 inches and 24.78 inches respectively. The 34-year average for these months was 24.4 inches. In 1921 there were only 6.85 inches of rain in the months of June and July as compared with 11.94 and 12.10 for the corresponding months in 1920 and 1922. The temperatures for these periods were not far different, the mean for the state for the months of June to September inclusive was 69.8°F. in 1920 and 71.7° and 70.5° for the same months for 1921 and 1922.

A series of field tests started in 1920 was continued in 1921 and 1922 to determine the residual effect of sulfur applications on both the yield of potatoes and the control of scab. The soil on which these tests were conducted is a sassafras loam which in 1919 had grown a crop of potatoes so scabby as to be almost entirely unsalable. A section of this field was divided into eightieth-

¹Paper No. 132 of the Journal Series New Jersey Agricultural Experiment Stations Department of Plant Pathology.

acre plots. In every case the sulfur applications were made just before the crop was planted. Soil samples were taken in the spring and fall of each year and their hydrogen-ion concentration determined. The results of one of these tests is presented in table 1. The figures given in the table represent the average of six untreated and three sulfured plots.

From the table it will be seen that the yield in 1921 on both the treated and check plots was greatly reduced as compared with that of 1920 and 1922. This decrease was the result of the dry season.

It will be observed likewise that scab was much more severe in this than in the other two years. In this connection it is interesting to note that on the untreated plots the number of unsalable tubers increased with a decreased rainfall. In 1920, 76.3 per cent of the crop was unsalable as compared with 87.2 and 99.3 per cent in 1922 and 1921. It will be recalled that the rainfall for the summer months in these three years was 29.21, 24.78 and 21.26 inches respectively. This is in entire accord with Sanford's conclusion that soil

TABLE 1
Relation of rainfall and soil acidity to the development of potato scab

YEAR	TREATMENT	RAIN-FALL APRIL- SEPTEM- BER	YIELD	CLEAN	SALA-	UNSALA-	REACTION
			in.	per acre	TUBERS	TUBERS	
			bu.	per cent	per cent	per cent	pH
1920	Check.....	29.21	238.1	1.6	22.2	76.3	6.8
1921	Check.....	21.26	77.0	0.0	0.7	99.3	6.4
1922	Check.....	24.78	230.7	0.0	12.5	87.2	6.7
1920	600 lbs. inoculated sulfur.....		226.2	64.7	25.7	9.5	4.8
1921	300 lbs. inoculated sulfur.....		77.6	10.4	48.9	40.7	4.8
1922	600 lbs. inoculated sulfur.....		250.6	79.4	19.1	1.5	4.2

moisture is an important factor in determining the severity of scab. These differences in the amount of scab were apparent despite the fact that, in the case of the check plots, the mean hydrogen-ion exponent values were slightly lower in 1921 than in the other two years, and on the sulfur plots the mean values in 1920 and 1921 were identical.

A consideration of the hydrogen-ion concentration values of the soils from treated and untreated plots indicates, however, that soil moisture is by no means the only contributory factor. In 1921 the mean pH value of the check plots was 6.4 and on these 99.3 per cent of the crop was unsalable. On the other hand, on the sulfur plots, with a pH value of 4.8, only 40.7 per cent of the tubers were unsalable. This difference, amounting to 58.6 per cent in the number of unsalable tubers must be attributed to the differences in acidity since, as these plots were adjoining, it may be assumed that there was little variation in soil moisture content. The same relation holds for 1920 and 1922. In these two years still greater decreases were recorded in the number of unsalable tubers on the treated as compared with the untreated plots.

The relation of soil acidity and moisture to scab infection is still further apparent from a consideration of the data from the sulfur plots in 1920 and 1922. In the former year 64.7 per cent of the crop was free from scab as compared with 79.4 per cent in 1922. In this case the recorded differences in the number of clean potatoes cannot be attributed to any difference in soil moisture content since in 1920 the rainfall in the summer months was 4.43 inches greater than in 1922.

From table 1 it will be observed that the pH values of these plots was 4.8 in 1920 and 4.2 in 1922. In this instance the decrease in the number of scabby tubers must be attributed to an increase in soil acidity and not to a lessened soil moisture content.

In a second test conducted in this same field, a similar relation was found to exist between acidity and scab infection. The results of this test are presented in table 2, the figures given representing averages of 6 check and 3 treated plots.

TABLE 2
Influence of rainfall and soil acidity on the development of potato scab

YEAR	TREATMENT	RAIN-FALL APRIL- SEPTEM- BER	YIELD PER ACRE	CLEAN	SALA-	UNSALA-	REA- CTION
				TUBERS	per cent		
		in.	bu.	per cent	per cent	per cent	pH
1920	Check.....	29.21	209.1	15.2	28.0	51.0	6.7
1921	Check.....	21.26	127.6	0.0	4.4	95.6	6.6
1922	Check.....	24.78	317.9	4.4	34.2	61.4	6.4
1920	300 lbs. inoculated sulfur.....		325.0	37.2	35.3	27.5	6.0
1921	300 lbs. inoculated sulfur.....		107.7	10.9	53.5	35.6	4.8
1922	600 lbs. inoculated sulfur.....		292.4	72.0	23.3	4.7	4.6

From the table it will be seen that here again scab was much more severe on both the treated and untreated plots in 1921 than in 1920 or 1922. On the plots treated with sulfur, 35.6 per cent of the crop was unsalable in 1921 and only 27.5 per cent in 1920, although the mean pH values were 4.8 in the former and 6.0 in the latter year. It is evident that soil moisture is a limiting factor in determining the amount of scab, but with the same moisture content the disease is very much reduced by increasing the soil acidity as is apparent from the fact that in 1921, on the sulfur plots, with a pH value of 4.8, the crop was 35.6 per cent unsalable, while on the check plots, with a pH value of 6.6, 95.6 per cent of the crop was unsalable.

In this test, as in the one previously discussed there was considerably less scab in 1922 than in 1920 on the plots treated with sulfur. In the former year, with a pH value of 6.0 only 37.2 per cent of the crop was clean, while in 1922, the pH value of these plots was reduced to 4.6 with a corresponding reduction in the number of scabby tubers, 72.0 per cent of the crop being clean.

GREENHOUSE EXPERIMENT, 1921-1922

In order to obtain more definite information on the question, an experiment was conducted in the greenhouse in the winter of 1921-1922 to determine the influence of soil moisture on the amount of scab and also its influence on the oxidation of sulfur. The soil used in this test was a sassafras loam taken from the field in which the tests previously discussed were conducted. Two series of 2-gallon jars were run, each consisting of 12 cultures, allowing for 4 replications of each of the moisture contents employed. On the basis of water-holding capacity, the per cent moisture contents of the various cultures were 30, 40, 50, 60, 70 and 80. The cultures in one of the series were run as checks while in the other series each culture received an application of sulfur at the rate of 900 pounds per acre. In addition, a 4-8-5 fertilizer mixture was added to all the cultures at the rate of 1500 pounds per acre. Each culture was weighed at frequent intervals during the progress of the experiment and the water lost through evaporation and transpiration replaced. The soil in the cultures made up to 70 and 80 per cent of the water-holding capacity was so wet that the seed pieces rotted and no readings were obtained.

In order to obtain vigorous plants in all of the cultures, twelve tubers of the Irish Cobbler variety were selected in the fall of 1921 from plants that were free from disease. The tubers were disinfected for 1.5 hours in a solution of 1-1000 mercuric chloride. Each of the tubers was then cut into two pieces weighing 41 gm. each and including three eyes; one of these pieces was planted in a culture treated with sulfur and the other in its check of the same moisture content. Soil samples were taken from each culture at time of planting and again at approximately 10-day intervals until the experiment was concluded; hydrogen-ion determinations were made by the colorimetric method at the time of sampling.

The experiment was started on November 18, 1921, and concluded February 24, 1922. Soil temperature readings were taken at 3-day intervals during the progress of the experiment. While the temperature in the low moisture cultures was higher than in those of high moisture content, the range was very small, the mean values being 24.38°C. and 23.95°C. respectively. At time of harvesting, the green weights of the tubers, the number of tubers showing scab, and the per cent of the surface of each that was scabbed was obtained. The results are presented in table 3. This table is divided into two sections. In section 1 is given the results from the check, and in section 2 the sulfur series. From the first column of section 1 it will be seen that with an increase in the soil moisture content, there was a marked increase in the weight of tubers harvested, while in the second column it will be seen that all of the tubers, regardless of soil moisture content, showed scab. It will be observed, however, that with each increase in soil moisture content, there was a decrease in the per cent of surface scabbed; in the cultures with highest moisture content, 38.5 per cent of the surface was scabbed as compared with 84.7 per cent in the culture with lowest moisture content.

In the series treated with sulfur, there was a marked decrease in the number of tubers showing scab as well as in the per cent of surface scabbed. In the cultures of low moisture content, 41 per cent of the surface of the tubers was scabbed as compared with 2.5 per cent of the surface of the tubers produced in the cultures of high moisture content. It is apparent that in this experiment, as in the field tests, soil moisture was a factor of considerable importance in determining the amount of scab; that this is not the only or the most important factor, however, is clear from a consideration of the pH values of these two series. The initial pH value of the soils in each culture in both series was 6.9. In the series receiving no sulfur, only slight differences were observed during the progress of the experiment, regardless of soil moisture content. On the other hand, in the sulfur series, at the time the second soil samples were taken, ten days after the sulfur application was made, the pH values decreased to 6.4. Similar decreases were observed on subsequent sampling until at the time the plants were harvested; the exponent value of the cultures with 30 to 60 per cent moisture content was uniformly 5.1.

TABLE 3
Influence of soil moisture and acidity on the development of potato scab

SOIL MOISTURE WATER HOLDING CAPACITY	NO-SULFUR SERIES				SULFUR SERIES			
	Weight of tubers per cent	Scabby tubers per cent	Amount of surface scabbed per cent	Reaction pH	Weight of tubers gm.	Scabby tubers per cent	Amount of surface scabbed per cent	Reaction pH
30	38.0	100	84.7	6.8	33.35	100	41.0	5.1
40	69.9	100	82.3	6.9	51.15	66.6	9.7	5.1
50	68.1	100	75.8	6.9	62.7	83.3	6.6	5.1
60	68.7	100	38.5	6.9	46.7	55.5	2.6	5.1

A comparison of sections one and two of table 3 shows that in every instance, regardless of soil moisture content, there was considerably less scab in the cultures with low than in those with high pH values. In those with the moisture content adjusted to 30 per cent of their water-holding capacity and with a pH value of 5.1, only 41.0 per cent of the surface was scabbed as compared with 84.7 per cent in the cultures with a pH value of 6.8. In the check cultures with highest moisture content, all of the tubers were infected with 38.5 per cent of the surface scabbed while in the cultures receiving sulfur only 55.5 per cent of the tubers were infected and these showed only 2.6 per cent of the surface scabbed. The mean pH values of these cultures was 6.9 and 5.1 respectively. In the light of these results it is evident that while soil moisture is an important factor in determining the amount of scab, soil acidity is of equal and probably of greater importance since with the same moisture content scab is less severe on soils with an acid than on those with an alkaline reaction.

REFERENCE

- (1) SANFORD, G. B. 1923 The relation of soil moisture to the development of common scab of potato. *In* *Phytopath.*, v. 13, no. 5, p. 231-236.

A MODIFICATION OF THE TRUOG SOIL ACIDITY TEST¹

F. W. PARKER AND J. W. TIDMORE

Alabama Polytechnic Institute

Received for publication May 31, 1923

The Truog soil acidity test (3) is widely used as a practical test for soil acidity but has had a limited use in research work. This is probably due to the fact that the test is not sufficiently quantitative for research purposes. It is difficult to detect small differences in acidity, especially among strongly acid soils, and more difficult to satisfactorily record the results. Despite these objections the method has given results that compare favorably with other methods (1), (2) and the authors have found the method useful for certain lines of work. In using the test as a means of indicating changes in acidity due to different soil treatments, it seemed desirable to modify it in such a manner as to overcome the two objections mentioned above. The modification as described in this paper makes possible a more accurate quantitative expression of the results of the test and affords a simple, rapid and accurate method of determining differences in soil acidity.

In the modified test the amount of hydrogen sulfide evolved on boiling the soil with Truog's reagent is accurately determined by titration with a standard solution of iodine instead of permitting it to react with a lead acetate paper. In order to secure a larger amount of hydrogen sulfide for the determination, the amount of soil used in making the test has been increased from ten to twenty grams and the time of boiling increased from two to three minutes. The procedure developed for making the modified test is as follows:

Weigh out 20 gm. of air-dry soil and place it in a 500 cc. Erlenmeyer flask, add 100 cc. of a one per cent solution of BaCl_2 containing, in suspension, 0.10 gm. of neutral ZnS . Place the flask on a wire gauze over a bunsen burner and connect with a 6-mm. glass delivery tube. The delivery tube is twice bent at right angles to form two parallel arms 10 cm. apart. The short arm is 5 cm. long and passes through a rubber stopper into the Erlenmeyer flask. The other arm is 41 cm. long and extends to within 3 cm. of the desk or when finally placed in position to within 1 cm. of the bottom of a 50-cc. graduated cylinder. After the contents of the flask have come to a boil and as soon as steam has been emitted from the long arm of the delivery tube for 10 seconds, the flask is raised and the delivery tube inserted into a 50-cc. graduated cylinder containing exactly 25 cc. of 4 per cent solution of NH_4OH . The cylinder must be in a bath of cold water which prevents the contents being raised to the boiling point. Boiling is continued for 3 minutes, after which the delivery tube is removed from the cylinder. The flame of the burner must be adjusted so that just 10 cc. of water will be distilled over in the 3 minutes of boiling. Remove the cylinder from the beaker, read and

¹ Published with the permission of the Director of the Alabama Experiment Station.

record the increase in volume which should be 10 cc. Transfer the solution to a 100-cc. beaker, add 10 cc. of 0.01 *N* iodine and 2 cc. of a freshly prepared starch indicator solution, acidify with 2 cc. of concentrated HCl. The excess of iodine is now titrated with 0.01 *N* Na₂S₂O₃, and the amount of H₂S evolved is calculated. One cubic centimeter of 0.01 *N* iodine is equivalent to 0.17 mgm. H₂S. Duplicate determinations should agree to within 0.02 mgm. H₂S.

EXPERIMENTAL

When using the quantities of soil and reagent recommended by Truog, the amount of hydrogen sulfide evolved during two minutes of boiling is so small in the case of slightly acid soils that it is apparent that the accuracy of the determination can be increased by modifying the test so that larger quantities of hydrogen sulfide are evolved. The following experimental results show the effect of varying amounts of soil, reagent and time of boiling on the amount of hydrogen sulfide secured in the determination.

Table 1 gives the amount of hydrogen sulfide evolved when different quantities of soil were used in making the test. In all instances 1.1 gm. of the re-

TABLE I

Hydrogen sulfide evolved in the modified Truog test when varying quantities of soil were used

AMOUNT OF SOIL USED	SOIL NO. 41		SOIL NO. 44	
	H ₂ S	H ₂ S	H ₂ S	H ₂ S
gm.	mgm.	relative amount	mgm.	relative amount
5	0.433	100	0.148	100
10	0.773	178	0.292	197
20	1.292	298	0.462	312
30	1.530	353	0.581	392

agent was used and boiling continued for three minutes at such a rate that 10 cc. of water was distilled over. The results are the averages of closely agreeing duplicates. According to the Truog test, soil 41 is very strongly acid and soil 44 is medium in acidity.

The results show that the evolution of hydrogen sulfide is greatly increased by increasing the quantity of soil. Twenty grams of soil was taken as a convenient amount to use in the modified test. Increasing the quantity of soil above 20 gm. did not greatly increase the amount of hydrogen sulfide evolved and the larger quantity increased frothing when boiling started.

Table 2 gives the amount of hydrogen sulfide evolved when different quantities of reagent were used in making the test. In these determinations 20 gm. of soil were used and boiling was for three minutes.

Increasing the quantity of reagent above 1.1 gm. the quantity recommended by Truog decreased the amount of hydrogen sulfide secured from the strongly acid soil and caused only a very small increased production from soil 44. This indicates that 1.1 gm. of the reagent, containing 1 gm. of barium chloride and 0.1 gm. of zinc sulfide, is the best quantity of the reagent to use in the

test. This quantity is accurately secured by taking 100 cc. of a 1 per cent solution of barium chloride containing, in suspension, 1 gm. of neutral zinc sulfide per liter. The suspension must be thoroughly shaken each time before measuring out the 100 cc.

The amount of hydrogen sulfide secured for a determination may be increased by absorbing the hydrogen sulfide evolved during a longer period of boiling than the two minutes recommended by Truog. However, prolonged boiling may be objectionable due to side reactions and alterations in the acidity of the soil. The influence of time of boiling on the quantity of hydrogen sulfide produced is shown in table 3. Twenty grams of soil and 1.1 gm.

TABLE 2

Hydrogen sulfide evolved in the modified Truog test when varying amounts of reagent were used

AMOUNT OF REAGENT USED gm.	SOIL NO. 45		SOIL NO. 44	
	H ₂ S mgm.	H ₂ S relative amount	H ₂ S mgm.	H ₂ S relative amount
0.55	1.278	100	0.374	100
1.1	1.351	105.7	0.462	123.5
2.2	1.249	97.7	0.476	127.2
3.3	0.909	71.1	0.479	128.0

TABLE 3

Hydrogen sulfide evolved in the modified Truog Test during successive one-minute intervals

PERIOD OF BOILING min.	SOIL NO. 41		SOIL NO. 44	
	H ₂ S mgm.	H ₂ S relative amount	H ₂ S mgm.	H ₂ S relative amount
1	0.4992	100.0	0.1907	100.0
2	0.4207	84.2	0.1496	78.4
3	0.3496	70.0	0.1252	65.6
4	0.3029	60.6	0.1122	58.8
5	0.2898	58.0	0.1028	53.9
6	0.2337	46.8

of reagent were used. The hydrogen sulfide evolved during successive 1-minute periods was determined. The results show that more hydrogen sulfide is evolved during the first 1-minute period than during any succeeding minute. The quantity evolved decreases with each successive period, the decrease being most marked in the second period. The relative decrease was very nearly the same for the two soils as can be seen from an inspection of the figures in the third and fifth columns of table 3. Three minutes is considered the most desirable length of time for boiling since it gives more hydrogen sulfide for the determination, is not long enough to permit side reactions to seriously interfere with the test, and during that time a convenient volume of water is distilled over.

Fifty soils have been tested by both the regular and modified Truog tests. The results of the two tests agree closely, as would be expected. When the soils were arranged in the order of their acidity they were placed in approximately the same order regardless of the method used. However, the modified test permitted a much better comparison and made evident differences that could not be detected with the test paper. For instance, the test papers for soils 15 and 4 appeared to be identical but according to the modified test 1.191 mgm. of hydrogen sulfide was evolved from soil 15 while 1.352 mgm. was evolved from soil 4. The test papers from soils 12, 24, 13 and 5 appeared identical, but the quantities of hydrogen sulfide evolved were 0.691, 0.700, 0.725 and 0.802 mgm. respectively. In general, with soils of slight and medium acidity, it is difficult to detect with the regular test differences in acidity corresponding to 0.075 or 0.100 mgm. of hydrogen sulfide as indicated by the modified test. If the soils are strong or very strong in acidity the test papers may not show differences corresponding to 0.200 to 0.300 mgm. of hydrogen sulfide. These results show that when the acidity of a number of soils is being compared, as has been done by Johnson (1) and Parker and Bryan (2), the modified test would be very useful.

SUMMARY

1. A modification of the Truog soil acidity test is proposed for use in research work.
2. The suggested modification consists of absorbing the hydrogen sulfide evolved in the test in dilute ammonia. An excess of standard iodine solution is then added, the solution acidified and the excess iodine is titrated with standard sodium thiosulfate of the same normality. The results of the test are recorded as milligrams of hydrogen sulfide evolved.
3. Increasing the quantity of soil used in making the test increases the amount of hydrogen sulfide evolved. Increasing the quantity of reagent above 1.1 gm. does not increase and may decrease the amount of hydrogen sulfide evolved.
4. The modified test affords a short, simple and accurate method of determining slight differences in soil acidity.

REFERENCES

- (1) JOHNSON, H. W. 1922 The relation of hydrogen-ion concentration in soils to their lime requirements. *In Soil Sci.*, v. 13, p. 7-23.
- (2) PARKER, F. W., AND BRYAN, O. C. 1923 Soil acidity as measured by sugar inversion, the Truog test and the hydrogen-ion concentration and its relation the hydrolysis of ethyl acetate. *In Soil Sci.*, v. 15, p. 99-107.
- (3) TRUOG, E. 1921 Testing soils for acidity. *Wis. Agr. Exp. Sta. Bul.* 312.

A COMPARISON OF THE JONES CALCIUM ACETATE METHOD FOR LIME REQUIREMENT WITH THE HYDROGEN-ION CONCENTRATION OF SOME QUEBEC SOILS

EVERETT A. CARLETON¹

Macdonald College, Quebec

Received for publication May 7, 1923

The problem of soil acidity is one that is common to most soils of humid regions. A large amount of investigation has been carried on to determine the nature of the phenomenon and to find a satisfactory method for its determination. The methods that have been advanced are many and vary greatly in principle and technique. These have been studied from time to time in relation to one another, and in relation to field conditions with the idea of selecting the most satisfactory, if any. MacIntire (15) has reviewed and cited the most important literature on the subject.

Lime requirement methods are intended to measure the total amount of base necessary to neutralize a soil; that is, to change the reaction to pH 7. Whether a particular method accomplishes this can only be determined by a consideration of the hydrogen-ion concentration. There are two means by which the hydrogen-ion concentration of a soil may be determined, viz; directly with the hydrogen electrode, and indirectly by the comparison of the color of the appropriate indicator in a standard solution with that of the same indicator in the aqueous extract of the soil. The former is more accurate, while the latter is simpler. Gillespie (6) was the first investigator to report comparisons of the two methods and he has shown fair agreement. Since that time one or the other of these procedures has been used by different workers in soil studies and for the investigation of lime requirement methods. Knight (13) studied a series of soils, the lime requirement of which had been previously determined by several different methods and determined their hydrogen-ion concentration with the hydrogen electrode. He used a type of electrode, however, which required the use of a neutral salt solution, so that his results are not comparable with others. Blair and Prince (1) and Joffe (10) studied the Veitch method from this viewpoint and found that soils (of one particular

¹ This investigation was conducted under a grant from the Honorary Advisory Council for scientific and industrial research and the present report is a portion of a thesis submitted to the Committee on Graduate Studies of the McGill University in partial fulfillment of the requirements for the Master of Science degree.

The writer wishes to express his appreciation for the helpful suggestions and criticisms tendered by Dr. J. F. Snell.

type) having a pH value of 6.7, or over, were alkaline by this method and that the hydrogen-ion concentration and the lime requirement in this case seemed to correlate. Johnson (11) using the same methods with soils of widely varying types, claims there is no correlation between the lime requirement as determined by the Veitch method and the hydrogen-ion concentration. The latter also studied the Truog zinc sulfide method. Fisher (5) used the colorimetric method and barium hydroxide for studying the Hutchison-MacLennan method. In 1920, W. H. MacIntire (14) Associate Referee of the Association of Official Agricultural Chemists, instituted a collaborative investigation of methods by different workers in America. The methods investigated were the freezing point method of Bouyoucos, the Tacke method, the MacIntire method and the hydrogen-ion concentration method. Other methods were to be investigated, among them the Jones calcium-acetate method, but the lack of sufficient cooperators prevented it. In his report to the association MacIntire recommended that the Jones method be studied. The features of this method are its simplicity, rapidity and adaptability. We have made it the subject of this investigation.

THE JONES CALCIUM-ACETATE METHOD FOR LIME REQUIREMENT

Connor (4) has studied the Jones method along with the Veitch, Hopkins and Hutchison-MacLennan methods on soils of different types. He found that the Jones and Hutchison-MacLennan methods were the most consistent in relation to one another, and that by using a factor for the former of 1.35 instead of 1.8, these two methods would give more concordant results. Stephenson in his study of soil acidity methods (18) seems to have overlooked the factor. Hill (8) used the Jones method for lime requirement determinations in investigating the effect of green manure on soil acidity. On comparing it with the Veitch method, he claims a fair agreement of the two. Burgess (2) in studying the effect of chemical fertilizers on the soil reaction with the hydrogen electrode, used this method for his lime requirement determinations. His is the only work that shows the relation between the lime requirement results by the Jones method and the hydrogen-ion concentration of the soil. Only acid soils were studied.

The Jones method is based on the formation of acetic acid by the addition of calcium acetate to a definite quantity of soil. The titratable acid is multiplied by the factor 1.8 to obtain the amount of acid equivalent to the corresponding weight of soil.

Jones had advanced two methods, viz., a standard method (12) and a field method (8). In this investigation, the field method was used for all determinations. Comparisons of the two in this laboratory have given close agreement and the field method has the advantage of being the simpler of the two.

Field method

Transfer 5.6 gm. soil to a 200-cc. flask, add 0.5 gm. calcium acetate and 150 cc. distilled water. Mix thoroughly and let stand 15 minutes, shaking at intervals of 2 or 3 minutes. Make up to volume of 200 cc., mix thoroughly and filter into a suitable flask or cylinder. Discard the first 10-15 cc. of filtrate, which may be cloudy. Titrate 100 cc. of the clear filtrate, using phenolphthalein as an indicator, with 0.1 *N* NaOH. This reading multiplied by 2 gives the cc. of 0.1 *N* alkali required to neutralize the acetic acid in 200 cc. of the solution. This figure times the factor 1.8 times 1000 equals the pounds of lime (CaO) required per 2,000,000 pounds of soil.

The correction for the calcium acetate used is determined by making the test as outlined above, using 0.5 gm. acetate without the addition of soil. It should not be over 0.2 cc. 0.1 *N* NaOH.

The standard method differs from the field method only in the treatment of the soil after weighing and before filtering. The same weight of soil and acetate are transferred to a mortar and mixed with a pestle. Sufficient water is added to make a fairly stiff paste, which is pestled for 20 seconds. Thirty cubic centimeters more of water are added and mixing continued for 30 seconds. The suspension is then washed into a 200 cc. flask, keeping the volume below 160 cc. This mixture is allowed to stand for 15 minutes, with frequent shaking as in the field method. From this point the procedure is the same for both methods.

Preparation of samples

Fifty-one samples of soil collected from different sections of the Province of Quebec were used in these studies. The samples were first air-dried by spreading them in thin layers over porcelain topped tables for several days. A uniform method for pulverizing the soil was adopted, which was thought not to present any new unweathered surfaces of the soil particles. The soil was rubbed in an unglazed porcelain mortar with a rubber-tipped pestle until no more passed through a sieve having circular openings one millimeter in diameter. The siftings were then thoroughly mixed and placed in a tightly sealed preserving bottle. The residue was weighed, recorded in per cent of total sample, and discarded. The lime requirement by the Jones method was determined on each soil as they were obtained, while the determinations with the hydrogen electrode were made later.

Unfortunately we have no system of soil classification in the Province of Quebec and very little has been done along this line. The description of types given in this article are estimates only, but are probably near enough for this purpose.

Apparatus for determining hydrogen-ion concentration

A discussion of the principles underlying the use of the hydrogen electrode is not within scope of this article. Such can be obtained from any text book on physical chemistry or from Clarke's book "The Determination of Hydrogen Ions" (3).

Various types and forms of apparatus have been devised by different workers for measuring the hydrogen-ion concentration. In setting up our arrangement (fig. 1), we tried to have it as simple and easily constructed as possible. No claim of originality is made for we have merely used parts of types advanced by others. The material used is common to all chemical laboratories. The electrode is patterned after Hildebrand (7) while the vessel is that used by Sharp and Hoagland (17). The hydrogen electrode consists of a piece of platinum wire, gauge 18, about $\frac{1}{8}$ inch long, sealed into the end of a piece of $\frac{1}{4}$ inch glass tubing so that about $\frac{1}{4}$ inch of platinum is exposed. A distillation test tube from which the bottom has been removed is used to envelop the electrode. The latter extends down through the tube, being held at the top by a rubber stopper, so that the exposed platinum is just visible below. The electrode was coated with platinum black at frequent intervals and stored in distilled water

when not in use. Hydrogen enters the side arm and leaves at the bottom passing through the solution. Connection is made between the unknown solution and the calomel electrode by an agar tube in the usual way.

Using the above arrangement we made measurements of standard buffer solutions prepared as recommended by Clark (3). The results given in table 1 were obtained with the first standard (pH 5.8) of the primary potassium phosphate series. The electrode was checked in this way at frequent intervals during the course of the work.

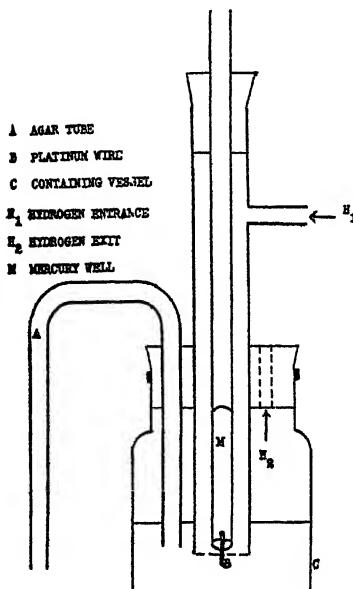


FIG. 1. HYDROGEN ELECTRODE AND VESSEL

TABLE 1

Electrode measurements of a standard solution

TIME	POTOMETER READINGS	LOGARITHM OF THE HYDROGLN-10 ^{-A} CONCENTRATION
minutes	millivolts	pH
5	626.5	5.81
10	627.0	5.82
15	627.0	5.82
20	627.0	5.82

The normal calomel electrode was used. The measurements were made with a Leeds and Northrup potentiometer, model 7655. This is a more suitable instrument for soil work than the expensive type K instrument. Hydrogen was prepared electrolytically from generators constructed like those used by Knight (13) using sodium hydroxide as electrolyte and iron electrodes. The hydrogen was washed twice with water before entering the electrode. No trouble was experienced which might be due to impure hydrogen.

DETERMINATION OF THE HYDROGEN-ION CONCENTRATION OF THE SOILS WITH
THE HYDROGEN ELECTRODE

Five grams of soil in 50 cc. of distilled water were used in all measurements with the hydrogen electrode. With this proportion of soil to solution, the equivalent of about 20 tons of calcium carbonate to 2,000,000 pounds of soil could be added as calcium hydroxide solution for lime requirement determinations. The soil was shaken constantly during the entire period of taking readings. Readings were made at intervals of five minutes as nearly as possible.

Results of the electrometric measurements are stated to the nearest hundredth of a pH unit; not that the accuracy is to that degree, but to show the relation between samples. Millivolt readings were converted to pH values by use of the table prepared by Schmidt and Hoagland (16). No effort was made to control the temperature. Measurements were made at room temperature, which was quite constant at 22°C. + 1°C.

The progress of the potentiometer readings in each determination was uniform except in a few cases as noted below. There was an increase for the first two or three readings after which constant readings were obtained for the remainder of the time. At first readings were made for one hour, but it was found that if three or four check readings were obtained at as many consecutive 5-minute observations, the same reading would be obtained for an hour at least. The exceptions that occurred were with a few very acid soils and some of those at, or near neutrality.

With six very acid soils the progress was an increase for the first ten minutes and then a decrease of a millivolt or less at each reading thereafter. Knight (13) and others have noted this and account for it as being due to more acid coming into solution or to hydrolysis.

In the case of the neutral or nearly neutral soils consecutive readings showed a progressive increase which was large for the first several measurements and of two or three millivolts in magnitude for the remainder of the period. The rapid increase in millivolts usually extended over a slightly longer time than was the case with the other soils, but readings taken at the twenty-minute point agreed closely with the colorimetric value. The reason for the changes noted is probably loss of carbon dioxide. That it would not be a factor in case of the more acid soils is brought out by the work of Hoagland and Sharp (9). These workers measured the hydrogen-ion concentration of soils with different pH values with various partial pressures of carbon dioxide and found that "the hydrogen-ion concentration of suspensions of acid soils is not markedly affected by increasing the content of carbon dioxide up to 10 per cent. The hydrogen-ion concentration of slightly alkaline soils is slightly increased by such treatments. A notable increase in hydrogen-ion concentration is observed when soils containing alkali carbonate are similarly treated."

SOIL		ELECTROMETRIC DETERMINATION	COLORIMETRIC DETERMINATION	DIFFERENCE
Number	Type	pH	pH	pH
4	Silt loam	4.85	4.3	+0.55
3	Silt loam	4.85	5.0	-0.15
10	Gravelly silt loam	4.90	4.8	+0.10
22	Gravelly fine silt loam	4.90	5.2	-0.30
8	Coarse gravel	4.94	5.4	-0.46
2	Gravelly fine silt loam	4.99	5.0	-0.01
6	Fine silt loam	5.02	4.7	+0.32
18	Fine sandy loam	5.06	5.1	-0.04
12	Fine silt loam	5.07	5.0	+0.07
11	Silt loam	5.11	5.2	-0.09
14	Gravelly fine silt loam	5.14	5.4	-0.26
29	Sandy loam	5.14	5.4	-0.26
16	Fine silt loam	5.14	5.1	+0.04
1	Gravelly fine silt loam	5.19	5.2	-0.01
20	Gravelly silt loam	5.19	5.1	+0.09
7	Silt loam	5.19	5.3	-0.11
13	Gravelly silt loam	5.26	5.3	-0.04
5	Silt loam	5.28	5.4	-0.12
34	Sandy loam	5.31	5.4	-0.09
26	Gravelly silt loam	5.36	5.4	-0.04
25	Fine sandy loam	5.36	5.5	-0.14
9	Silt loam	5.38	5.3	+0.08
21	Fine sandy loam	5.41	5.4	+0.01
30	Fine sandy loam	5.41	5.4	+0.01
17	Fine silt loam	5.44	5.4	+0.04
19	Very fine sandy loam	5.44	5.4	+0.04
15	Silt loam	5.48	5.45	+0.03
24	Silt loam	5.56	5.2	+0.36
31	Very fine sandy loam	5.56	5.3	+0.26
23	Gravelly silt loam	5.65	5.6	+0.05
28	Fine sandy loam	5.70	5.6	+0.10
35	Sandy loam	5.77	5.7	+0.07
32	Gravelly fine silt loam	5.95	5.8	+0.15
39	Silt loam	6.02	6.2	-0.18
27	Silt loam	6.02	6.0	+0.02
43	Fine sandy loam	6.04	6.0	+0.04
33	Gravelly silt loam	6.15	6.0	+0.15
37	Medium sand	6.19	6.3	-0.11
44	Sandy loam	6.34	6.4	-0.06
42	Sandy loam	6.37	6.35	+0.02
45	Silt loam	6.39	6.45	-0.06
40	Fine sandy loam	6.56	6.5	+0.06
46	Fine sandy loam	6.56	6.6	-0.04
38	Fine sandy loam	6.58	6.4	+0.18
41	Silt loam	6.63	6.7	-0.07
36	Gravelly silt loam	6.66	6.6	+0.06
47	Silt loam	6.96	7.0	-0.04
49	Sandy loam	7.0	7.0	0.00
48	Silt loam	7.02	7.0	+0.02
50	Silt loam	7.27	7.2	+0.07
51	Silt loam	7.61	7.6	+0.01

TABLE 3
Lime Requirement Determinations

SOIL NUMBER	INITIAL LIME REQUIREMENT <i>lbs. per acre</i>	REACTION AFTER TREATMENT <i>pH</i>
4	14,120	6.9
3	16,400	6.9
10	10,600	7.0
22	5,440	7.1
8	11,900	7.0
2	17,600	6.8
6	12,500	6.8
18	6,100	6.9
12	10,600	6.7
11	10,600	7.0
14	9,920	7.0
29	4,500	7.0
16	8,350	6.8
1	21,120	6.8
20	5,780	7.1
7	11,240	6.8
13	10,600	7.0
5	13,600	6.8
34	3,530	7.3
26	4,820	7.3
25	5,140	7.0
9	11,240	7.0
21	5,780	6.9
30	3,850	6.9
17	7,680	6.8
19	5,780	6.9
15	8,350	6.9
24	5,460	7.0
31	3,850	7.1
23	5,460	7.1
28	4,500	7.1
35	3,530	7.3
32	3,850	7.0
39	2,890	7.1
27	4,820	7.0
43	2,250	6.9
33	3,850	7.1
37	3,210	7.1
44	2,250	7.0
42	2,570	7.3
45	2,250	7.2
40	2,890	7.2
46	1,930	7.2
38	3,090	7.1
41	2,890	7.2
36	3,530	7.1
47	1,600	7.7
49	960	7.3
48	1,280	7.4
50	960	7.8
51	640	8.2

COLORIMETRIC DETERMINATION OF THE HYDROGEN-ION CONCENTRATION OF THE SOILS

Standards for the colorimetric measurements were prepared according to the outline given by Clark (3). The procedure for making measurements differed very little from that used by Gillespie (6). We used 50 grams of soil in 100 cc. of distilled water. The mixture was shaken for a minute, allowed to settle for a short time and clarified by centrifuging for 15-20 minutes. The comparisons were made in the six compartment comparator. The standards were checked electrometrically to insure accuracy.

Compared with the electrometric measurements, the colorimetric values show good agreement. The greatest difference is 0.55 of a pH unit in the case of soil 4. The remaining differences (table 2) are as follows: with three soils, the readings differed by more than pH 0.3; with three soils, by pH 0.2-0.3; with ten soils, by pH 0.1-0.2; and with 34 soils, by less than pH 0.1.

LIME REQUIREMENT BY THE JONES METHOD AND HYDROGEN-ION CONCENTRATION

The results of lime requirement determinations are stated in terms of calcium carbonate required for 2,000,000 pounds of soil. These values are calculated by means of the factor 1.8 (table 3).

There was no direct correlation between the hydrogen-ion concentration and lime requirement by the Jones method. However, high lime values were always associated with a low pH, although the converse did not hold. The lighter soils had a lower lime requirement than the heavier ones, and of the lighter types, those with the higher hydrogen-ion concentration had the greater requirement for lime. Had our classification of the soil types been more accurate, these statements would probably be more obvious than they appear. If this is true the litmus paper test for soil acidity or Wherry's (19) field method for determining the hydrogen-ion concentration of soils would have some value in showing the need for lime after the soil type had been determined.

An important point that these measurements bring out, is that the Jones method gives a lime requirement for neutral and slightly alkaline soils. An explanation of this is not difficult when it is considered from the viewpoint of the hydrogen-ion concentration. Phenolphthalein begins to show color at pH 8.5 and gives a gradation of color up to pH 10.5 according to Clark (3), so that all titrations with this indicator are carried to some point in this range. A titration of the calcium acetate in water is used as a blank to correct for impurities in the salt. It might appear to correct also for the indicator but the difference in buffer action of the two solutions prevents this. Another way of stating it is that the presence of the extracted materials in the filtrate gives that solution a greater "reaction inertia." To illustrate:

Five-tenths gram calcium acetate dissolved in 200 cc. water gives a pH value of 6.9-7.0. One hundred cubic centimeters of this solution requires 0.05 cc. 0.1 N NaOH solution to give a slight pink to phenolphthalein. The clear filtrate of soil 49 prepared according to the

Jones method, requires 0.2 cc. 0.1 N NaOH to give the same color to this indicator. This gives a value for lime of 960 pounds per acre. The discrepancy is emphasized by the factor but still it exists. For soils 47 and 48 it is even greater. Further evidence of this fact is brought out by an experiment with some soils treated in the laboratory with calcium carbonate as indicated by the Jones method to neutralize the acidity. The procedure follows.

Three soils from the Macdonald College Farm were dried and sifted through a 2.5-mm. sieve. The pH values, carbonate carbon, and lime requirement by Jones method were determined. Results are given in table 4.

Calcium carbonate was added to each soil equivalent to the amount indicated by the Jones method and a slightly larger amount in a second portion. One-kilogram portions of soil were used in each case. The soil and calcium carbonate were well mixed, placed in glass receptacles, and maintained at optimum moisture content for 5 weeks. All the soil was then spread out to dry, and finally stored in sealed glass jars until measurements were made. The pH value, residual carbonate and lime requirement were determined.

TABLE 4

Effect of calcium carbonate on the hydrogen-ion concentration and lime requirement of slightly acid soils

SAMPLE NUMBER	CaCO ₃ ADDED PER KGM. SOIL	REACTION		0.1 N NaOH EQUIVALENT OF CARBONATE CARBON PER GM. SOIL		CaCO ₃ REQUIREMENT BY JONES METHOD PER KGM. SOIL	
		Original	Final	Original	Final	Original	Final
		gm.	pH	gm.	gm.	gm.	gm.
11	1.548	6.58	7.0	0.63	0.71	1.548	0.410
11a	1.750	6.58	7.15	0.63	0.70	1.548	0.410
14	0.900	6.63	6.9	0.48	0.48	0.900	0.640
14a	1.200	6.63	7.0	0.48	0.48	0.900	0.640
27	1.890	6.31	6.8	0.58	0.48	1.890	0.735
27a	2.200	6.31	6.9	0.58	0.68	1.890	0.735

These results show that the calcium carbonate was practically all decomposed and the carbon dioxide set free. The resulting hydrogen-ion concentration was close to neutrality in practically all cases. The excess calcium carbonate was probably used up to neutralize the nitric acid produced during nitrification. These soils after such treatment still have a "lime requirement" by the Jones method. The only logical explanation of this has been stated above.

LIME REQUIREMENT INDICATIONS BY THE HYDROGEN ELECTRODE

As a test of the constancy of the factor used in this method, we determined electrometrically the hydrogen-ion concentration resulting from the treatment of each soil with the quantity of lime water indicated by the Jones method. The lime water was prepared by allowing a large excess of calcium hydroxide to stand in water for six months with frequent shaking. In this way we obtained a fully saturated solution. Analysis by precipitation gave a value of 2.363 mgm. per cc. calculated as calcium carbonate. This solution showed a trace of magnesium in 50 cc. that was too small to weigh. Five grams of soil was used as in the determination of the original pH value. With this weight of soil, 2.115 cc. standard lime water solution prepared and analyzed as above

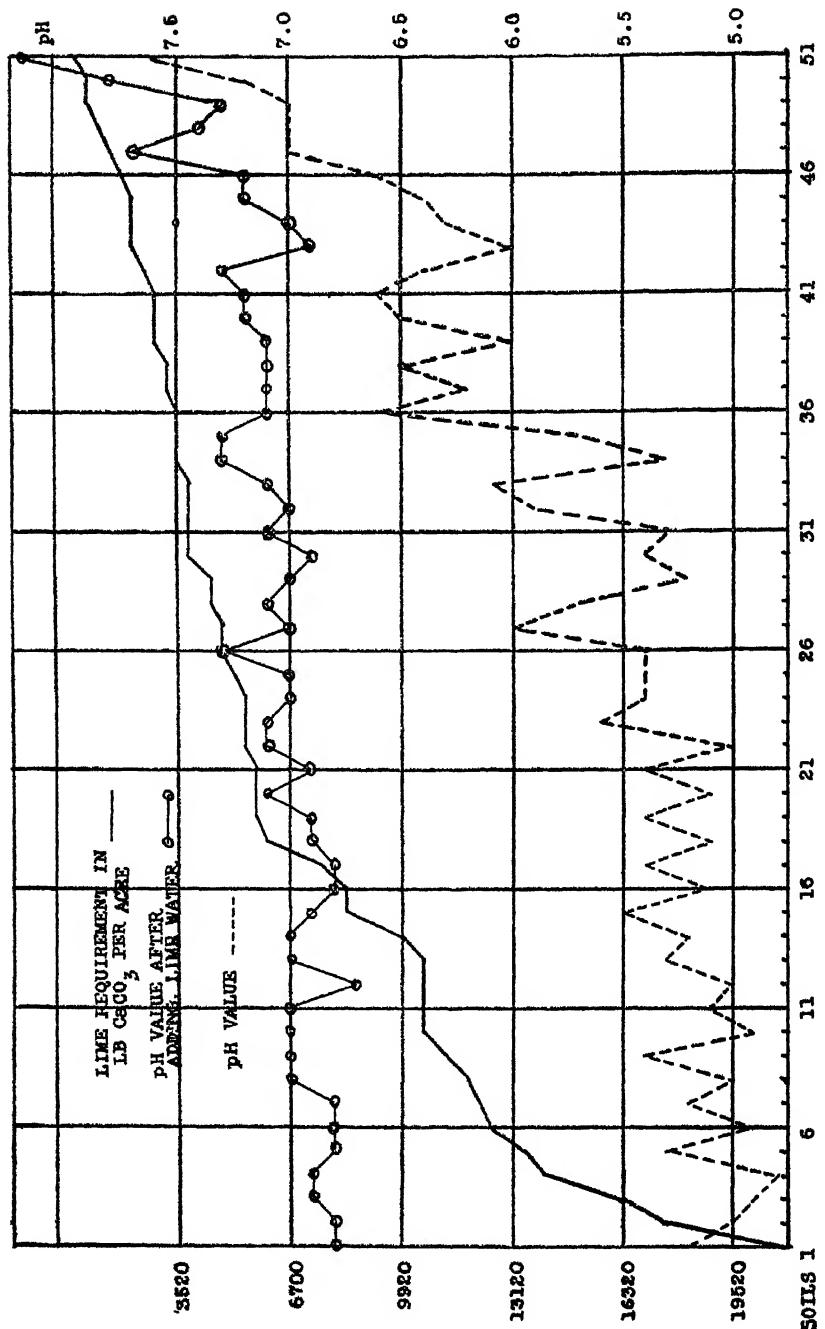


FIG. 2. SOILS ARRANGED IN ORDER OF INCREASING LIME REQUIREMENT AND PLOTTED FOR ORIGINAL REACTION, REACTION AFTER TREATMENT, AND LIME REQUIREMENT

should be added to equal an application of a ton of ground limestone to 2,000,000 lbs. of soil. The additions of lime solution were made as indicated by the Jones requirement, the volume made up to 50 cc. and the suspensions shaken for one hour before the hydrogen-ion concentration was determined. Knight (13) has shown that the reaction between the calcium hydroxide and soil is practically completed at the end of this time. For the determination of the hydrogen-ion concentration the procedure was the same as in the case of determining the original pH values, i.e. readings were taken at 5 minute intervals. A rapid increase in millivolts occurred for the first two or three readings and very small increases (a millivolt or two) were observed in the subsequent readings. For the sake of uniformity the fifth reading was used in all cases.

In figure 2 we have plotted the values obtained as described above against the soils arranged in order of increasing lime requirement. This brings out the fact that in general the factor is a function of lime requirement and correlates to a less extent with the pH value. In general those soils having a requirement of three tons of ground limestone or greater would require a factor of 1.8 or more, while those of a smaller requirement would demand a factor less than this. This generalization applies more to the heavier soils than to the sandy type. With the latter, the value after treatment is generally high so that we should take as a factor for these soils a figure below 1.8.

SUMMARY

1. Good agreement between the electrometric and the colorimetric methods for determining the pH values of fifty-one Quebec soils was obtained.
2. Some correlation between hydrogen-ion concentration and lime requirement by the Jones method seems to hold in a general way for soils of the same type.
3. The Jones method gives a lime requirement for neutral and slightly alkaline soils up to a reaction of about pH 7.6. This is caused by the indicator used and the increased "buffer" effect of the soil extract over that of the blank.
4. Soils treated with lime water as indicated by the Jones method gave values which were in general close to neutral. Soils of high lime requirement were generally still slightly acid, while those of low requirement were usually slightly alkaline.

REFERENCES

- (1) BLAIR, A. W., AND PRINCE, A. L. 1920. The lime requirement of soils according to the Veitch method, compared with the hydrogen-ion concentration of the soil extract. *In Soil Sci.*, v. 9, p. 253.
- (2) BURGESS, P. S. 1922. The reaction of soils in the field as influenced by the long continued use of fertilizer chemicals. *R. I. Agr. Exp. Sta. Bul.* 189.
- (3) CLARK, W. M. 1922. The Determination of Hydrogen Ions. Williams and Wilkins Co., Baltimore.
- (4) CONNOR, S. D. 1917. Lime requirement of some acid soils. *In Jour. Assoc. Off. Agr. Chem.*, v. 3, p. 139.

- (5) FISHER, E. A. 1921 Studies on soil reaction. II. The colorimetric determination of the hydrogen-ion concentration in soils and aqueous soil extracts. *In Jour. Agr. Sci.*, v. 11, p. 45-65.
- (6) GILLESPIE, L. J. 1916 The reaction of soil and measurements of hydrogen-ion concentration. *In Jour. Wash. Acad. Sci.*, v. 6, p. 7.
- (7) HILDEBRAND, J. H. 1913 Some appliances of the hydrogen electrode in analysis, teaching and research. *In Jour. Amer. Chem. Soc.*, v. 35, p. 847.
- (8) HILL, H. H. 1919 A comparison of methods for determining soil acidity. *Va. Agr. Exp. Sta. Tech. Bul.* 19.
- (9) HOAGLAND, D. R., AND SHARP, L. T. 1918 The relation of carbon dioxide to soil reaction as measured by the hydrogen electrode. *In Jour. Agr. Res.*, v. 12, p. 139.
- (10) JOFFE, L. H. 1920 Hydrogen-ion concentration measurements of soils in connection with their "lime requirements." *In Soil Sci.*, v. 9, p. 261.
- (11) JOHNSON, H. W. 1922 The relation of hydrogen-ion concentration in soils to their lime requirement. *In Soil Sci.*, v. 13, p. 7-22.
- (12) JONES, C. H. 1915 Method for determining the lime requirement of soils. *In Jour. Assoc. Off. Agr. Chem.* v., 1, p. 43-44.
- (13) KNIGHT, H. G. 1920 Acidity and acidometry of soils, 11. *In Jour. Indus. Engin. Chem.*, v. 12, p. 457.
- (14) MACINTIRE, W. H. 1920 Report on the lime requirement of soils. *In Jour. Assoc. Off. Agr. Chem.*, v. 4, p. 108-123.
- (15) MACINTIRE, W. H. 1921 Soil acidity with regard to its quantitative determination. *In Jour. Amer. Soc. Agron.*, v. 13, p. 137-162.
- (16) SCHMIDT, C. L. A., AND HOAGLAND, D. R. 1919 Table of pH, H^+ and OH^- values corresponding to electromotive forces determined in hydrogen electrode measurements. *Univ. Cal. Pub. in Physiol.*, v. 5, no. 4, p. 23.
- (17) SHARP, L. T., AND HOAGLAND, D. R. 1916 Acidity and adsorption in soils as measured by the hydrogen electrode. *In Jour. Agr. Res.*, v. 7, p. 123.
- (18) STEPHENSON, R. E. 1918 Soil acidity methods. *In Soil Sci.*, v. 6, p. 33-52.
- (19) WHERRY, E. T. 1920 Soil acidity and a field method for its measurement. *In Ecology*, v. 1, p. 160.

THE LITMUS METHOD FOR DETECTING THE SOIL REACTION

EVERETT A. CARLETON

Macdonald College

Received for publication May 31, 1923

INTRODUCTION

Litmus paper is widely used as a qualitative test for acid soils. Bailow (1) has cited the opinions of a number of different authorities as to its value, while Karraker (5) has shown by experiment the great variation in sensitivity which may occur in test paper obtained from different sources. The most systematic study of the behavior of litmus paper in the presence of acids of different strengths is that contributed by Walpole (6) in 1913. He found that blue litmus paper had basicity varying in different papers. This basicity gave the paper a certain "reaction inertia" in dilute solutions of acids. For this reason litmus paper in dilute solutions of highly dissociated acids is incapable of showing the true reaction.

Harris (4) believed that the change in the color of blue litmus paper was due to the selective adsorption of the soil for the base of the blue litmus salt, leaving the red dye on the paper. He supported his belief by citing the fact that in the majority of cases the aqueous extract of acid soils does not redden blue litmus paper. Gillespie and Wise (3) refuting this claim, have shown that the reason the aqueous extract of acid soils does not usually affect blue litmus paper is that such a solution is not buffered strongly enough to overcome the basic nature of the test paper. They show this by comparing the behavior of blue litmus paper in a dilute solution of hydrochloric acid of hydrogen-ion concentration equal to that frequently occurring in the aqueous extract of soils, with that in a well buffered solution of the same hydrogen-ion concentration, for example one of the 0.05 M phthalate series.

THE SENSITIVITY OF BLUE LITMUS PAPER

If azolitmin or litmus paper were as sensitive an indicator as those which have been recently prepared for use in the colorimetric determination of the hydrogen-ion concentration, we should have the ideal indicator for soil work. The range as given by Clark (2) is pH 4.5-8.3. This the writer found to be quite true for the particular paper used in this work. Blue litmus paper in contact with an acid soil is slowly changed in color. The speed and completeness of the change undoubtedly depend both on the degree of acidity (hydrogen-ion concentration) and the buffer or reserve acidity present. In other words, the change would seem to depend upon the total acidity as well as the pH value. To determine which of these seemed to have more influence on the change in color of the litmus paper was the object of this experiment.

The blue litmus paper used was a commercial one, purchased from the Will Corporation, Rochester, N. Y. To determine its usefulness for the particular work, we measured its sensitivity in a dilute, highly dissociated acid

against the color change produced in a series of standards of varying pH that were prepared for colorimetric comparisons according to Clark (2). Hydrochloric acid was used as the highly dissociated acid and the solution was prepared as outlined by Gillespie and Wise (3) by diluting 0.5 cc. of approximately 0.2 *N* acid to one liter. This solution, measured colorimetrically with methyl red indicator against the 0.05 *M* phthalate series, proved to have pH 4.0.

Four buffered solutions were used as standards and had the following pH values: 6.8, 6.4, 6.0, 4.2. A strip of blue litmus paper was placed in each of these four solutions, and also in the hydrochloric acid. The shade of color on the litmus paper in the standards was assumed immediately in each case and altered only slightly on standing. The change in the case of the litmus in the hydrochloric acid solution was slow and did not reach its proper coloration in three hours. Results are given in tables 1 and 2.

TABLE 1
Approximate color assumed by litmus paper in standard solutions

pH 6.8	pH 6.4	pH 6.0	pH 4.2
Lavender	Very slightly pink	Slightly pink	Pink

TABLE 2
The shade of color and indicated pH values of the litmus in the HCl solution

		TIME OF OBSERVATION				
	Immedi-ately	10 min.	20 min.	30 min.	3 hrs.	
Color observed	No change	Laven-der	Very slightly pink	Very slightly pink.	Slightly pink	
Corresponding pH value.....		6.8	6.4	6.4-6.0	6.4-6.0	

This paper appeared to be very sensitive to buffered solutions and had some degree of sensitiveness in a dilute solution of a highly dissociated acid. It was therefore judged sufficiently sensitive for the work.

THE TESTING OF SOILS WITH BLUE LITMUS PAPER

Twenty-two soils, the pH values of which were determined both electrometrically and colorimetrically, were used. The soils varied widely as to color and other physical characteristics. The pH value of these soils ranged from 4.8 to 6.7.

The blue litmus paper used was the same as that from which the above results were obtained. The sheets were cut in strips $\frac{1}{4}$ - $\frac{3}{8}$ inch wide and made short enough to lie flat across the bottom of 100-cc. beakers. Over the test

paper was placed one thickness of coarse white filter paper cut to fit snugly in each beaker. The paper was dampened with distilled water, and about 10 gm. of a given soil were placed in the beaker. Enough distilled water was then added to moisten the soil, avoiding an excess. The entire series of soils was prepared in this way and allowed to stand one half hour before making the comparisons. At the end of this time the beakers were turned on their sides with the bottoms towards the observer. The different beakers

TABLE 3
of soils by litmus test compared with pH value and lime requirement

SOIL NUMBER	ORDER OF ARRANGEMENT BY FIRST OBSERVER	ORDER OF ARRANGEMENT BY SECOND OBSERVER	pH VALUE	LIME REQUIREMENT BY JONES METHOD PER ACRE
14	1	1	5.11	9,900
22	2	4	4.90	5,400
1	3	6	5.19	21,120
2	4	3	5.00	17,600
10	5	7	4.85	10,600
6	6	2	5.02	12,500
3	7	5	4.85	16,400
25	8	9	5.36	5,410
34	9	12	5.31	3,500
26	10	14	5.36	4,800
31	11	8	5.36	3,850
19	12	11	5.44	5,780
17	13	10	5.44	7,680
20	14	16	5.19	5,780
23	15	13	5.65	5,460
28	16	17	5.70	4,500
35	17	15	5.77	3,530
32	18	19	5.95	3,850
39	19	18	6.02	2,890
36	20	21	6.66	3,530
40	21	20	6.56	2,890
62	22	22	6.43	2,890

were then arranged without consulting the numbers, according to the shade of litmus paper, to give a gradation of color from blue to pink. The arranging was done by two observers, one of whom knew nothing of the pH values.

DISCUSSION

Taking into account the arrangement of these soils by the two observers, the soils can be divided into three groups and each group will contain the same soils although the order is not the same. The first seven soils make up the first group; the next ten, the second group; the remaining five, the third group.

The color assumed by the litmus paper in each case could be roughly described as pink, slightly pink and very slightly pink with pH values of 4.8-5.2, 5.2-5.8 and 5.8-6.7, respectively. The general conclusion of the experiment would then be that the color of litmus paper in contact with the soil depends on the hydrogen-ion concentration of the soil. Thus this simple test may be used to obtain some approximate idea of the intensity of the acidity.

Frequent reference is made in the literature to the behavior of certain soils toward red litmus paper. In this case the change takes place more slowly and so is less definite. However, certain soils have been described as basic to red litmus paper and the expression needs explanation.

Samples of red litmus paper in this laboratory appear to vary in shade which means that the pH the particular paper is indicating is different. The different papers were judged to vary from pH 4.5 to 6.0. This being the case, it is apparent that theoretically any soil with a pH value greater than that of the paper would cause a change in color toward the basic shade so that a soil may be acid and still cause a change on red litmus paper. Since the usual method for detecting change in litmus paper is by comparison with either a portion of the same strip not in contact with the soil or with another strip of the same paper as a blank, the change in the paper may not necessarily mean a soil is acid. The actual shade of color assumed must be taken into account.

SUMMARY

1. It has been shown that the litmus paper test depends on the hydrogen-ion concentration of the soil.
2. The three shades of color assumed by blue litmus paper in contact with these soils may be roughly described as pink, slightly pink and very slightly pink with pH ranges of 4.8-5.2, 5.2-5.8, and 5.8-6.7, respectively.
3. It is further pointed out that the changing of color of red litmus does not mean a soil is basic unless the proper color (blue) is imparted to the paper.

REFERENCES

- (1) BARLOW, J. T. 1916 Soil acidity and the litmus paper method for its detection. *In Jour. Amer. Soc. Agron.*, v. 8, p. 23.
- (2) CLARK, W. M. 1922. The determination of hydrogen-ions, p. 94, 99-109. Williams and Wilkins, Baltimore, Md.
- (3) GILLESPIE, L. J. 1918 The action of neutral salts on humus and other experiments on soil acidity. *In Jour. Amer. Chem. Soc.*, v. 40, p. 796.
- (4) HARRIS, J. E. 1914 Soil acidity and methods for its detection. *In Sci.* 40, 492.
- (5) KARRAKAR, P. E. 1918 The value of blue litmus paper from different sources as a test for soil acidity. *In Jour. Amer. Soc. Agron.*, v. 10, p. 180.
- (6) WALPOLE, G. S. 1913 The use of litmus paper as a quantitative indicator of reaction. *In Biochem. Jour.*, v. 7, p. 260-267.

SOIL PROFILE STUDIES IN MICHIGAN

M. M. McCOOL, J. O. VEATCH AND C. H. SPURWAY¹

Michigan Agricultural Experiment Station

Received for publication May 23, 1923

A new concept of soils, in their genetic and geographic relationships, is gaining acceptance among American soil scientists. The fundamental basis and principles underlying this concept originated among Russian workers and have been most comprehensively presented by Glinka (3). In America the principles have been promulgated by Marbut (4) of the United States Bureau of Soils and further the broad scheme has been modified and adjusted for a practicable detailed classification of soils, the principles established, and the criteria stated by him for the recognition of the soil unit.

Soils in their broader relationships are a function of climate. Geology, topography and native vegetation are locally modifying factors. Two important factors of soil formation are the moisture or drainage conditions under which the soils have developed and the time or period through which the soil forming processes have operated. Thus there are two great taxonomic groups: (1) relatively old or mature soils developed under conditions of good drainage; (2) relatively old or mature soils developed under poor drainage. A third group of soils in which the profile is incomplete must be recognized, namely those which are very recent and practically equivalent to geological formations. In such cases, the upper part of the formation or that part which influences plant growth is described in soil terms.

In this scheme of soil classification, the soil profile includes the whole thickness, upon which the soil-forming processes have operated, from the surface down to the parent rock or geologic substratum. The importance of a separation of a profile into its *natural divisions* is emphasized, and the classification is based upon *intrinsic* soil characteristics.

On the basis of this concept of soils and soil classification, field and laboratory studies of soils in Michigan have been undertaken and the preliminary results obtained during the year 1922 are herewith presented.

The primary purpose has been to ascertain chemical and physical facts regarding the soils; to determine whether basic chemical and physical constitutional differences exist between separate members or horizons of the soil

¹ The field observations and interpretation of soil profiles are largely the work of Veatch and McCool; the hydrogen-ion studies and interpretations of the results are the work of Spurway. Credit for laboratory determinations by others is given in the proper place.

profile and to what extent the visible phenomena in the field can be correlated with laboratory data.

In the geographic studies, the observations in the field seem to justify the division of the state into two soil provinces which we are designating for the present simply as northern and southern. From the nature of things a transition or blending of the soils of the two groups would be expected, but it is impracticable at present, at least, to attempt to draw boundaries for a transitional group or to define a typical profile for such a group. The generalized profiles of the two groups are given below.

PROFILE FOR THE NORTHERN GROUP

(Fairly well to well drained mature soils)

1. Mold
Humous soil (very thin)
2. Gray or podsolized horizon (3-24 inches)
3. Brown horizon (dark coffee-brown to light leather-color and dull yellow; thickness of 4 inches to 4 feet; horizon of acid concentration)
4. Horizon showing iron oxide coloration, red or yellow; highest clay content; gradation to substratum
5. Substratum.

The thickness of the whole soil layer or complete profile in general is 30 to 48 inches; in the case of the most impervious clays it may not be more than 24 inches, while in the case of some of the most pervious sands it may be as much as 6 feet

PROFILE FOR THE SOUTHERN GROUP

(Well drained mature soils)

1. Mold and humous soil
2. Brownish or yellow horizon
3. Horizon of maximum clay and colloids and maximum intensity of coloring from iron oxide
4. Decrease in iron coloring and decrease in clay content or colloids. Gradational. Small thickness
5. Substratum

Section 3 of this generalized profile for the southern group corresponds to section 4 of the profile for the northern group.

Profile for Sands

1. Mold—very thin. (Gray sand, a very thin and inconspicuous horizon in certain situations)
2. Brownish humous soil very thin
3. Dull yellow sand. Horizon of maximum clay and colloids
4. Decrease in intensity of iron oxide coloring. Small thickness
5. Substratum

Profile for Heavier Soils

1. Mold and humous soil
2. Brown or yellowish horizon
3. Horizon of leaching or light colored soil
4. Maximum clay, or maximum compactness and plasticity. Gradation to
5. Substratum high in basic and aluminic rocks and minerals

Horizon no. 3 of the heavier soils is not a true podsolized horizon.

A great number of sub-groups and types may be recognized upon the basis of differences in thickness, texture, structure, consistency and chemical character, but all have the generalized profiles as stated.

The laboratory data have been assembled in tables 1-4.

Discrepancies and inconsistencies appear of which some are easily explainable because of errors in field and laboratory procedure, while others stand as negative and refutive for the present. But the authors feel justified on the basis of present field and laboratory investigations in drawing the following conclusions and presenting the following theories as a basis for further work.

In the typical northern profile, the surface horizon of virgin soils is obviously one of accumulation, and the higher contents of calcium, magnesium, nitrogen and phosphorus which appear here are believed to be due mainly to organic matter or organic compounds containing these elements. Beneath this layer of mold soil, the soil forming processes appear to be those of eluviation or removal of the more soluble and finer particles, progressively from the surface downward, as indicated by the relatively higher proportion of silica in the upper part of the profile and increase in calcium and magnesium carbonates with depths. However, in the northern profile, there appears to have been developed as a subsequent or later phenomenon a brownish or yellowish horizon, one of organic accumulation and of concentration of acids, a horizon much more definitely marked and more strongly developed than in the southern profile.

It is the presence of the acid layer in a definite position in the profile and the strongly marked gray or podsolized horizon which chiefly distinguishes the typical northern from the typical southern profile. The gray layer appears to have resulted from leaching and it is assumed that organic acids infiltrating from the layer of surface mold have played a strong part in its development. The relative amount of silica in the gray horizon appears to be higher than in the soil horizons below; the content of iron and alumina are fairly consistently higher in the brown horizon than in the gray; the nitrogen content is highest in the surface, lower in the gray horizon, with an upward trend in the curve for the brown horizon, and again a downward trend to the substratum. This condition seems to be true also in a measure for phosphorus. There is no conclusive evidence of any concentration of calcium and magnesium or other bases in the horizon no. 3, so far as can be determined from the total chemical analysis.

Horizon no. 3 is perhaps the most puzzling feature of the profile in chemical nature and origin. The brownish or yellowish color is either in large part or entirely organic in nature and organic colloidal matter is certainly present. The nature of the organic compounds is not known and their determination would probably be a most complex and intricate undertaking. The cause for their concentration at a certain position in the profile is equally obscure. An alkaline (KOH) solution of the brown matter shows iron, alumina, and silica; calcium and magnesium may be present or may be practically absent. This

TABLE I
Analyses of northern and transitional soils

LABORATORY NUMBER	HORIZON	SiO ₂ <i>per cent</i>	FeO ₃ <i>per cent</i>	Al ₂ O ₃ <i>per cent</i>	P ₂ O ₅ <i>per cent</i>	CaO <i>per cent</i>	MgO <i>per cent</i>	Na ₂ O <i>per cent</i>	K ₂ O <i>per cent</i>	SO ₃ <i>per cent</i>	N <i>per cent</i>	MnO <i>per cent</i>	TiO ₄ <i>per cent</i>	H ₂ O <i>per cent</i>	IGNITION LOSS <i>per cent</i>	CO ₂ <i>per cent</i>
3001*	1	91.65	0.96	3.24	0.14	1.06	0.68	0.08	0.83	0.00	0.20	0.01	0.05	0.02	0.00	0.00
3002	2	92.55	0.68	2.03	0.12	0.73	0.64	0.00	0.41	0.01	0.05	0.01	0.02	0.00	0.00	0.00
3003	3	90.11	1.18	3.73	0.14	0.51	0.58	0.51	1.82	0.00	0.02	0.00	0.02	0.00	0.00	0.00
3004	4	94.61	0.68	2.33	0.09	0.45	0.57	0.00	0.52	0.00	0.007	0.00	0.00	0.00	0.00	0.00
3005*	1	90.47	1.34	4.75	0.20	0.98	0.65	0.04	1.50	0.06	0.17	0.02	0.03	0.00	0.00	0.00
3006	2	92.73	1.22	4.93	0.19	0.61	0.53	0.06	1.05	0.02	0.03	0.02	0.02	0.02	0.02	0.02
3007	3	92.98	1.00	4.83	0.17	0.65	0.59	0.02	1.21	0.02	0.02	0.02	0.02	0.02	0.02	0.02
3008	4	92.27	0.76	3.77	0.07	0.49	0.62	0.00	1.25	0.00	0.01	0.00	0.00	0.00	0.00	0.00
3019*	1	85.50	0.64	1.85	0.09	0.59	0.27	0.03	0.64	0.05	0.28	0.02	0.02	0.02	0.02	0.02
3020	2	94.92	0.44	1.15	0.04	0.24	0.28	0.12	0.60	0.02	0.02	0.02	0.02	0.02	0.02	0.02
3021	3	90.40	1.40	2.99	0.09	0.32	0.37	0.30	0.92	0.02	0.07	0.02	0.02	0.02	0.02	0.07
3022	4	89.88	1.14	3.28	0.09	0.46	0.45	0.31	0.93	0.03	0.05	0.03	0.03	0.03	0.03	0.05
3023*	1	74.69	0.98	3.32	0.19	0.63	0.71	0.31	0.37	0.15	0.47	0.04	0.04	0.04	0.04	0.47
3024	2	93.34	0.22	2.13	0.07	0.27	0.42	0.67	0.24	0.04	0.01	0.04	0.04	0.04	0.04	0.01
3025	3	86.64	0.76	4.48	0.05	0.36	0.36	0.96	1.03	0.06	0.06	0.06	0.06	0.06	0.06	0.06
3026	4	89.97	0.80	2.17	0.04	0.28	0.30	0.85	0.99	0.03	0.01	0.03	0.03	0.03	0.03	0.01
3053†	2	82.75	1.43	4.70	0.07	1.65	1.55	1.38	2.76	0.19	0.04	0.03	0.63	0.55	2.42	0.20
3054	3	64.85	4.90	9.38	0.07	2.30	2.98	1.63	3.55	0.15	0.05	0.12	0.40	2.60	6.85	0.22
3055	4	55.41	5.45	10.33	0.15	4.50	4.60	1.06	3.70	0.21	0.06	0.16	0.50	3.04	10.82	3.83
3056	Sub	40.04	3.95	7.11	0.12	15.73	6.50	1.64	2.65	0.17	0.04	0.10	0.62	2.03	18.29	15.23
3035*	1	98.05	0.72	2.93	0.07	0.81	0.34	0.28	0.72	0.06	0.13	0.03	0.03	0.03	0.04	0.00
3036	2	92.11	0.56	1.34	0.04	0.50	0.30	0.00	1.15	0.03	0.04	0.03	0.03	0.03	0.03	0.01
3037	3	91.00	1.00	3.91	0.10	0.67	0.54	0.00	1.02	0.03	0.01	0.03	0.03	0.03	0.03	0.01
3038	4	96.38	0.82	3.32	0.05	0.70	0.53	0.04	1.04	0.05	0.00	0.00	0.00	0.00	0.00	0.00

* Analysis by P. S. Brundage, Michigan Agricultural College.

Analysis by O. B. Winter, Michigan Agricultural Experiment Station.

horizon in nature varies from 2 or 3 inches in thickness to as much as 4 feet, from an obscure yellow coloration to very dark brown; it appears at 6-30 inches from the surface. Where the sands prevail there is the most marked development in general, where the highest aluminic conditions are at present there is the least thickness and most obscure development.

TABLE 2
Analyses of southern soils

LABORATORY NUMBER	HORIZON	SiO ₂ per cent	FeO ₃ per cent	Al ₂ O ₃ per cent	P ₂ O ₅ per cent	CaO per cent	MgO per cent	Na ₂ O per cent	K ₂ O per cent	SO ₃ per cent	N per cent	MnO per cent	TiO ₂ per cent	H ₂ O per cent	IGNITION LOSS per cent	CO ₂ per cent
3015	1	88.47	0.43	3.23	0.07	0.41	0.28	0.04	0.93	0.07	0.17					
3016	2	94.50	0.52	2.57	0.04	0.41	0.26	0.05	0.90	0.03	0.03					
3017	3	93.15	0.56	3.30	0.06	0.41	0.30	0.44	1.02	0.02	0.03					
3018	4	92.69	0.60	3.19	0.04	0.49	0.30	0.32	1.10	0.03	0.00					
3027*	1	86.38	0.76	1.65	0.16	0.34	0.29	0.43	1.08	0.06	0.24					
3028	2	89.28	1.22	3.60	0.12	0.44	0.72	0.65	0.37	0.05	0.05					
3029	3	91.92	1.02	3.72	0.06	0.49	0.45	0.57	0.41	0.06	0.02					
3030	4	92.66	0.96	3.71	0.08	0.46	0.49	0.78	0.42	0.06	0.00					
3031*	1	78.51	2.10	7.04	0.34	1.08	0.58	0.57	1.38	0.11	0.27					
3032	2	80.78	2.54	6.98	0.15	0.76	0.64	0.42	1.67	0.06	0.04					
3033	3	77.91	3.37	8.58	0.10	0.91	0.89	0.59	1.47	0.05	0.03					
3034	4	76.39	6.17	8.02	0.15	0.98	1.03	0.64	1.27	0.04	0.01					
3067*	1	74.60	2.10	1.85	0.22	1.73	1.95	1.30	1.82	0.62	0.21	0.15	0.28	1.98	10.33	1.87
3068	2	77.40	2.80	5.18	0.12	1.85	2.03	1.22	2.00	0.08	0.08	0.12	0.48	1.30	5.16	0.32
3069	3	76.85	3.65	4.48	0.09	1.78	2.10	1.12	1.97	0.05	0.05	0.31	0.53	1.82	5.70	0.07
3070	4	87.01	2.50	2.08	0.05	1.85	1.43	1.14	1.54	0.07	0.02	0.08	0.45	0.38	1.89	0.15
3071†	1	68.77	2.25	1.89	0.14	2.20	2.40	0.99	2.14	0.23	0.40	0.25	0.57	2.74	15.38	0.27
3072	2	77.20	3.10	3.60	0.08	1.85	1.90	1.11	2.39	0.24	0.11	0.15	0.40	1.40	6.40	0.19
3073	3	76.08	3.80	7.04	0.06	1.13	1.70	1.08	2.64	0.18	0.05	0.22	0.60	1.35	4.53	0.18
3074	4	70.14	3.70	10.91	0.07	1.68	2.35	0.94	2.58	0.14	0.04	0.14	0.40	1.61	5.31	0.37
3075	Sub	56.13	3.80	6.83	0.08	9.60	5.05	0.97	2.61	0.24	0.03	0.15	0.54	1.04	12.71	10.45

* Analysis by P. S. Brundage, Michigan Agricultural College.

† Analysis by O. B. Winter, Michigan Agricultural Experiment Station.

If it is true in general, as it appears to be, that the more calcareous and more clayey soils exhibit the least marked development of horizon no. 3, a possible explanation is that a larger proportion of the humic acid is combined with calcium and magnesium to form the less soluble humates, whereas with the sandier and less basic soils there is not sufficient calcium and magnesium to hold the organic acids at the surface and these filtrate downward and at certain points in the profile are precipitated or flocculated. Sodium, potas-

TABLE 3
Description of soils in northern and transitional group

LABORATORY NUMBER	HORIZON	REACTION	LIME REQUIREMENT	UNFREE WATER [†] (DILATOMETER)	HEAT OF WETTING [†]	SOIL DESCRIPTION
		pH	lbs.*		cal.‡	
3001	1	6.12	960	2.3	125.40	Transitional soil, deep dry sand. Horizon 3 not markedly developed as to the brown organic matter. Horizon 4 includes a part of the substratum. Virgin soil, but in old cut-over forest
3002	2	6.71	120	1.3	43.45	
3003	3	6.51	320	1.4	52.75	
3004	4	5.83	240	0.5	13.19	
3005	1	6.73	600	2.2	94.25	Transitional soil, sand. Brown horizon, no. 3, obscurely developed, substratum clay. Sample from a depth of 5 feet.
3006	2	5.93	400	0.9	50.62	Virgin soil, but in old cut-over forest
3007	3	5.93	400	0.7	37.58	
3008	4	5.92	280	1.1	24.17	
3009	Sub	6.71	600	
3019	1	5.60	1600	3.3	153.03	Typical northern profile, well drained sand; horizon 2 is 10-12 inches in thickness; horizon 3, brown color from organic matter, strongly marked
3020	2	4.58	600	0.8	20.67	
3021	3	4.65	3200	1.5	69.80	
3022	4	4.94	2240	
3022 [‡]	Sub	5.63	600	
3023	1	5.06	5200	4.4	155.35	Marked development of brown horizon, no. 3. Sand soil; poor drainage
3024	2	4.89	560	0.7	16.82	
3025	3	4.48	8040	1.4	140.08	
3026	4	4.82	1220	0.8	28.87	
3026 [‡]	Sub	5.28	400	
3039	1	7.46			Loam soil; typical northern profile; brown horizon no. 3, is 6 to 8 inches from the surface. No. 4 and substratum, previous, reddish, calcareous clay
3040	2	6.41	360			
3041	3	5.14	1560			
3042	4	7.47			
3043	Sub	8.25			
3044	1	4.31	7000	4.4	186.79	Sandy soil, poor drainage; virgin unburned accumulation or organic matter at surface.
3045	2	4.28	320	0.5	14.97	Marked development of brown horizon
3046	3	4.28	8000	2.4	159.96	
3047	4	4.99	720	0.1	16.55	
3048	2	5.29	640	0.7	16.23	Sandy soil and sand substratum; dry and well drained. Obscure development of brown horizon
3049	3	5.12	960	1.0	37.84	
3050	4	5.28	280	0.5	7.64	
3051	Sub	5.17	200	0.5	7.47	
3057	1	5.43	1520	1.8	62.62	Dry sandy soil. Horizon 2, only 2-3 inches in thickness, not typical podsol, contains a considerable percentage of organic matter
3058	2	4.77	1240	1.3	38.54	
3059	3	4.85	1240	1.1	40.55	
3060	4	4.99	520	1.1	17.90	
3061	Sub	5.28	400	0.4	10.37	

* Calcium required to bring two million pounds of soil to the neutral point.

† Dilatometer and heat of wetting determinations made by A. G. Weidemann.

‡ Calories of heat produced per 50 gm. of soil.

TABLE 3—Continued

LABORATORY NUMBER	HORIZON	REACTION	LIME RE-QUIRE-MENT	UNFREE WATER [†] (DILA-TOMETER)	HEAT OF WETTING [†]	SOIL DESCRIPTION
		ϕH	Ibs.*		cal.‡	
3035	1	5.95	920	2.2	87.18	Transitional soil, well drained, loose sand throughout; brown horizon, no. 3 poorly developed. Virgin soil, cut-over forest
3036	2	4.82	800	1.1	29.58	
3037	3	4.92	1000	1.1	29.33	
3038	4	5.00	320	0.7	18.67	
3076	1	6.07			265.30	Fairly typical northern soil; sandy loam, well developed brown horizon, 6-8 in. in thickness, gravelly substratum alkaline
3077	2	5.36			23.56	
3078	3	5.31			57.20	
3079	4	5.46			11.34	
3081	1	7.51			609.80	Virgin soil, horizon 1, first 2 inches of forest mold; well marked brown horizon 24 inches in thickness; substratum at 48 inches calcareous sand
3082	2	6.44			40.79	
3083	3	5.28			98.63	
3084	Sub	7.13			12.49	
3085	1	7.49			781.10	Very high percentage of organic matter in horizon 1. Well marked brown horizon 3, beginning at 12 inches; substratum, sand, gravel clay mixture, pervious calcareous
3086	2	6.95			39.15	
3087	3	5.88			53.54	
3088	Sub	7.73			41.35	
3089	1	7.22			571.90	Light sandy loam, well drained; horizon 2 contains a high percentage of organic matter than is typical; fairly well developed horizon. Sand and gravel, pervious substratum
3090	2	6.68			89.69	
3091	3	5.73			45.22	
3092	Sub	7.17			13.77	
3094	1	5.11			Dry sand, horizons 2 and 3 both poorly marked in the profile. Loose quartz sand substratum
3094½	2	4.94			33.85	
3095	3	4.94			27.66	
3096	4	5.34			23.00	
3097	Sub	5.70			9.20	
3097½	1	4.56			492.20	Dry sand; horizons 2 and 3 well marked and 10 and 12 inches in thickness respectively. Sample 30101 represents substratum at 12 feet
3098	2	5.66			10.37	
3099	3	5.02			40.45	
3100	4	5.39			16.72	
30101	Sub	5.65			5.40	
30102	1	4.51			198.56	Transitional soil, well drained loose sand.
30103	2	4.26			46.67	Horizons 2 and 3 obscurely marked in the profile
30104	3	4.89			32.37	
30105	4	5.48			11.26	

TABLE 3—Continued

LABORATORY NUMBER	HORIZON	REACTION	LIME REQUIREMENT	UNFREE WATER [†] (DILATOMETER)	HEAT OF WETTING [†]	SOIL DESCRIPTION
		pH	lbs.*		cal.‡	
30106	1	7.27			Old dune sand; brown horizon 3 conspicuously marked, reaching a thickness of 4 feet. Sample 30109 from a depth of 6 ft.
30107	2	5.43			4.56	
30108	3	5.41			40.02	
30109	Sub	7.57			10.01	
30110	1	4.78			Sand soil, poor drainage; horizon 3 a dark color, and slightly cemented
30111	2	4.65			18.15	
30112	3	4.60			121.72	
30113	4	5.31			34.12	

sium and nitrogen should show an increase in the third horizon. The chemical analyses afford a measure of evidence to support the above theory.

As the pH data show (5) considerable differences exist in the reaction of the various horizons of the soil profiles. The surface horizon may be acid or alkaline but the second and third horizon was found to be acid even in the limestone soils. The degree of acidity becomes less as the substratum or parent material is approached, or the reaction may be alkaline if limestone is encountered in quantities sufficient to exert its effects on the fine soil material.

It is evident from these results that the reaction of the profiles, or of the separate horizons, is not a determinative factor in the formation of these soil profiles, and that podsolization may take place in acid or alkaline soils; however, there appears to be an acid limit, which is in the region of pH 4.3. The reaction of these horizons is considered to be the result of chemical actions accompanying soil formation processes, and not a contributing cause of these processes.

As to the nature of the soil compounds causing the acid reaction of the several horizons, little is known at present. The specific cause of the reaction itself is undoubtedly the ratio between concentrations of hydroxyl and hydrogen ions in the soil solutions. In case of the typical northern group of podsolized soils there is a concentration of an acid substance or substances in the third or brown horizons as shown by their high lime requirements; but in the case of the transitional and southern groups, we have no positive data to show, whether the increased acidity of the second or third horizons is due to accumulation of acids or removal of bases; both factors may be operating with varying degrees of intensity. The possibility of a change in chemical composition affecting the solubility of the chemical components of these horizons must also be considered. Whatever may be said regarding the causes of the reaction of soils, we maintain that a specific reaction is the resultant of all its contributing causes, and as these causes vary in effect the soil reaction varies accordingly.

TABLE 4
Description of soils in southern group

LABORATORY NUMBER	HORIZON	REACTION	LIME REQUIREMENT	UNFREE WATER (DILATOMETER)	HEAT OF WETTING	SOIL DESCRIPTION	
						pH	lbs.
3015	1	5.43	1840	1.8	75.67	Loose, dry sand, loose sand substratum,	
3016	2	4.87	760	0.5	27.66	surface, virgin, unburned forest mold	
3017	3	4.87	800	0.9	19.15		
3018	4	6.10	120	0.6	4.50		
3027	1	4.82	2320	2.7	109.32	Well drained sand; mature or old soil.	
3028	2	4.43	1560	1.4	49.96	Horizon 3 in the sample includes a greater	
3029	3	5.33	720	0.8	20.53	thickness than properly belongs to it.	
3030	Sub	4.94	440	0.8	17.29	Substratum a loose incoherent sand	
3031	1	6.32	1160		179.42	Loam soil, well drained. Horizons 3 and 4	
3032	2	5.43	1160		65.52	friable reddish clayey horizons, with	
3033	3	5.19	1320		121.94	maximum clay in horizon 3. Substratum	
3034	4	5.33	1120		123.91	coarse, contains horizon limestone and	
3034	Sub	basic rocks	
30118	1	5.55			129.52	Old, well drained sand soil. Horizon 3	
30119	2	5.12			59.77	slightly loamy, barely coherent. Sand	
30120	3	5.63			36.63	and gravel substratum below 4 feet	
30121	4	5.39			23.26		
30122	1	6.05			133.53	Sandy loam soil, no. 3, lightest color	
30123	2	5.41			32.35	and apparently maximum leaching. No.	
30124	3	5.31			24.07	4, strongly cohesive reddish sandy clay,	
30125	4	5.53			90.36	18 inches in thickness. Substratum,	
30126	5	7.39			18.35	gravelly, sandy, calcareous	
3067	1	4.23			153.64	Dark colored loam, high content of humus	
3068	2				112.55	in surface soil; horizon 3 compact sandy	
3069	3				135.39	clay; horizon 4 at 36 to 48 inches, sand	
3070	4				39.10	and gravelly, includes part of substratum	
3071	1				235.38	Well drained heavy soil; horizon 2 at 4 to	
3072	2				106.31	8 inches a gray floury silt; horizon 3	
3073	3				114.88	mottled plastic clay; horizon 4 pale	
3074	4				142.98	yellowish clay; substratum, clay from a	
3075	Sub				104.46	a depth of 4 ft.	

The practical significance of these reaction results should not be overlooked. The degree of reaction or chemical composition of the surface horizon may be no indication of the reaction or composition of the underlying horizons; also they may not indicate adaptation to plant growth. A plant may extend its roots into one or more horizons, and thus grow in soils varying in reaction from alkaline to acid, in soils with various degrees of acidity, or in soils varying greatly

in chemical composition. It is evident in this connection that the soil profile as a whole is the unit to be considered in questions of plant adaptation or soil management. In scientific investigations pertaining to soils, it is also evident that soils should be sampled with respect to soil profiles and their horizons and not on the basis of linear depths alone.

In discussing the lime requirement data, consideration should be given to the fact that they refer to horizons of virgin soil profiles that vary greatly in thickness and represent effects of extreme conditions of soil formation; hence these results can not consistently be compared to the lime requirements of surface cultivated soils. In case of the southern and transitional groups, no marked increase in lime requirement is shown by the "no. 3" horizons over the others and, in general, the lime requirement diminishes in magnitude with depths. In the typical northern profiles, however, a marked accumulation of acids is shown in the third horizons and also in the surface humus layers except in case of the soil no. 3039, in which there is clearly an influence by limestone.

The heat of wetting (1) determinations show fairly consistent differences for the different horizons recognized in the field. It is believed that these determinations reflect differences in the amounts of organic and colloidal matter present, of active matter as opposed to the more inert crystalloid matter, and of unfree water (2). The heat of wetting is highest for the surface horizon, decreases for horizon no. 2, increases for horizon no. 3, and thence shows a uniform decrease with depth to the substratum.

In the typical southern profile, the surface horizon of the virgin soil is one of accumulation and accretion as in the northern profile, but beneath this the process seems to be one of eluviation. The progressive increase in calcium and magnesium carbonates with depth and the sandier and less clayey nature of horizon no. 2 afford evidence of this. There is no conclusive evidence so far either in the field observations or in the laboratory determinations of a horizon of concentration or accumulation formed either through precipitation of downward moving soluble matter or through mechanical translocation. No one horizon maintains consistently a maximum or minimum degree of acidity or alkalinity, but in the case of the heavier soils, where the layer of clay or maximum colloid content reaches its most marked development, there is a suggestion that the highest degree of acidity may prevail in a leached subhorizon resting directly upon the clay layer.

The nitrogen shows a consistent decrease from the surface downward, that is, there is no consistent rise in any horizon beneath the humous soil. The iron and alumina are highest in horizon 3 and 4 in the profile of the heavier soils. On the assumption that the soil compounds of these elements are the more acid and more insoluble, they would persist longer under the action of leaching processes. The theory is offered that as no. 3, or the layer of maximum clay and colloids, is decreasing in thickness and undergoing transformation through removal of its constituents, no. 4 and the upper part of the

substratum are concurrently changing to the nature of no. 3, through the action of soil weathering or soil forming processes. In the mature soil, possibly, an equilibrium has been established. The leaching process in soil formation becomes more marked in proceeding southward in the United States, as the mean temperature becomes higher and the summer rainfall greater, until it reaches an extreme in Florida.

The heat of wetting is high in the surface horizon, evidently because the accumulation of organic matter, and highest in horizon no. 3, where it apparently bears a relation to the maximum clay or active inorganic colloidal matter.

The laboratory investigations as far as they have progressed point to fairly consistent physical and chemical differences for the separate horizons as they have been interpreted in field studies. The authors believe that such profile studies as here outlined constitute a step forward in soil science. The profile study of soils will revolutionize the methods of sampling soil and as pointed out by Marbut (2) give a new meaning and value to analytical work. Further, it compels a new evaluation of soil in ecologic studies, since the soil assumes added importance as a factor when the chemical and physical differences of the separate horizons are studied in relation to root development. It places soil study on a natural basis and in fact lays the foundation of a new science which we might name, *podology*.

REFERENCES

- (1) BOUVOCOS, G. 1918 Relationship between the unfree water and the heat of wetting of soils and its significance. *Mich. Agr. Exp. Sta. Tech. Bul.* 42.
- (2) BOUVOCOS, G. J. 1922 Relation between heat of wetting, moisture equivalent and unfree water. *In Soil Sci.*, v. 14, no. 6, p. 431-434.
- (3) GLINKA, K. 1914 Die Typen der Bodenbildung, Berlin. Verlag von Gebruder Borntraeger.
- (4) MARBUT, C. F. 1920 Contributions of soil surveys to science. *Proceedings 41st Annual Meeting, Society for the Promotion of Agricultural Science*, p. 116-142.
- (5) SPURWAY, C. H. 1922 Studies on active bases and excess acids in mineral soils. *Mich. Agr. Col. Exp. Sta. Tech. Bul.* 57.

COMPARATIVE EFFECTS OF MURIATE AND SULFATE OF
POTASH ON THE SOIL IN A LONG CONTINUED
FERTILIZER EXPERIMENT¹

F. W. MORSE

Massachusetts Agricultural Experiment Station

Received for publication June 18, 1923

Field B of the Massachusetts Agricultural Experiment Station has been used since 1893 for comparing the effects of muriate of potash and sulfate of potash on crop production. The field contains 10 plots of $\frac{1}{8}$ acre each, which are numbered from 11 to 20 inclusive. Those with odd numbers have received muriate of potash and those with even numbers, the sulfate. Descriptions of the experiments and results are given in the annual report of this station in the annual reports for the years 1918 to 1923.

During the first 7 years, each potash salt was applied annually at the rate of 400 lbs. per acre; but since 1900, the quantity has been 250 lbs. Nitrogen and phosphoric acid have been supplied in ground bone at the rate of 600 lbs. per acre annually. In addition to the potash salts and bone, all the plots have received applications of lime; but the quantities and time of application have varied with different pairs.

The plots have been compared in pairs, 11 with 12, 13 with 14, 15 with 16, 17 with 18, and 19 with 20. Two pairs of plots have seldom been planted with the same crop in one year and every pair has borne a variety of crops during the experiment. The two salts have differed some in their effects on crops. Sulfate of potash has proved superior in production with more crops than muriate. A difference in the tints of the foliage upon a pair of plots was sometimes striking. Raspberries showed more winter injury on their muriate plot, and on one occasion an early frost severely injured squash vines on another muriate plot while on the adjoining sulfate plot the leaves were scarcely touched.

On account of the long continued use of the two distinct salts on these plots, Director Brooks deemed it important to know whether any cumulative effects had developed in the composition of the soil, which would distinguish one series from the other. Three pairs of plots were selected, 11 and 12, 15 and 16, 17 and 18, and samples of the soils were secured in November, 1915, after 22 successive applications of the fertilizers. Each plot was sampled by making numerous borings with an auger to the depth of seven inches.

¹ Published by permission of the Director of the Massachusetts Agricultural Experiment Station.

When air-dry, the soil was sifted through a standard sieve with 1-mm. holes, and the fine material used for chemical analysis. The soil has been classified as Merrimac sandy loam (5, p. 158).

Not much information was expected from an analysis by the common method of solution with HCl of sp. gr. 1.115, but two composite samples prepared respectively from the soils of the muriate plots, 11, 15 and 17, and sulfate plots, 12, 16 and 18, were analyzed with the results shown in table 1. The analytical work was executed by Mr. C. L. Beals.

The results are closely parallel and show the uniformity of the two series in composition. The widest proportional difference is with sodium oxide, but it should be borne in mind that this determination is the most difficult one of the series to keep free from errors, so no especial significance can be attached to the difference.

TABLE 1
Composition of soils of field B

CONSTITUENTS	PLOTS 11, 15, 17 TREATED WITH MURIATE	PLOTS 12, 16, 18 TREATED WITH SULFATE
Silica and insoluble matter.....	85.31	84.86
Potassium oxide.....	0.14	0.13
Sodium oxide.....	0.21	0.15
Calcium oxide.....	0.50	0.49
Magnesium oxide.....	0.69	0.72
Manganese oxide.....	0.09	0.10
Iron oxide.....	2.58	2.49
Aluminum oxide.....	4.14	4.19
Phosphoric anhydride.....	0.12	0.12
Sulfuric anhydride.....	0.08	0.08
Volatile matter.....	5.35	5.65

The samples from the individual plots were next analyzed by methods which might show whether the important bases, potassium, calcium and magnesium, differed in the solubility of their compounds on the two series. Standard fusion methods were used to determine total K₂O, CaO and MgO, while 0.2 N HNO₃, and distilled water were each used to determine their soluble forms, as both solvents have been often used in soil-studies. Sufficient soil and solvent were used to permit concentration of the solution and gravimetric determination of each constituent.

The only noticeable differences between the two series of soils, analyzed plot by plot, were that total lime and available lime were uniformly a trifle higher in the muriate soils than in the sulfate soils. The results of the analyses are averaged in the table. Potash was practically alike in both soils, and the amount soluble in 0.2 N acid was so small that no determination of its solubility in water was attempted. The magnesia results were also closely alike.

The quantities of lime that these plots had received were not uniform in amount or year of application. Plots 11 and 12 received 3000 lbs. hydrated lime per acre in 1910; plots 15 and 16 received 2000 lbs. per acre in 1905 and again in 1915; plots 17 and 18 received only 2000 lbs. per acre in 1915. The water-soluble lime was closely alike in all the soils, and this was also shown later by the reaction of the solutions.

The magnesia results by each method are practically alike on the two series and are small in quantity by the two solvents.

In spite of the well known difference in solubility of calcium chloride and calcium sulfate, which should be formed by the action of the respective potash fertilizers on the lime in the soil, the lime appears to have been removed less by the muriate than by the sulfate of potash treatment.

When the solubility effect of rain-water is considered, there is reason to expect both compounds of calcium to be completely removed annually, insofar as they are produced by the action of the potash salts. The less soluble CaSO₄ dissolves in water at 18° at the rate of 2.016 parts in 1000 (2). An

TABLE 2

Potash, lime and magnesia in the soils of field B by different methods, expressed in percentage of dry soil

	K ₂ O		CaO		MgO	
	Muriate soil	Sulfate soil	Muriate soil	Sulfate soil	Muriate soil	Sulfate soil
Total by fusion.....	per cent	per cent	per cent	per cent	per cent	per cent
1.84	1.81	1.91	1.68	1.06	1.09	
Available by 0.2 N HNO ₃	0.012	0.011	0.175	0.162	0.028	0.037
Soluble in water.....			0.0105	0.0106	0.0047	0.0050

acre-inch of water should weigh 226,875 pounds and be capable of dissolving over 450 pounds of the substance. The application of 250 lbs. of sulfate of potash cannot produce more than 195 lbs. calcium sulfate. Therefore, a season's rainfall and percolation should completely remove the calcium compounds formed by the action of the respective potash fertilizers applied in the spring, whether as sulfate or as chloride.

Further study of the comparative effects on the lime of the soil was made by determining the lime requirements of the different plots. It has already been mentioned that each pair of plots had received a different amount of lime from either of the other pairs. The determinations were made by Mr. Beals and both the Veitch (4) and the Hopkins (1, p. 20) methods were used.

Plots 11 and 12 showed like results by both methods. Plots 15 and 16 differed somewhat, and it was noted when the samples were prepared by sifting that the one from 16 contained visible particles of lime. This pair of plots was bearing raspberries, which had interfered with thorough surface tillage. The second application of lime was made in the spring of the year

in which the samples were taken. The lower lime requirement on plot 16 is attributed to possible difference in tillage rather than to the lesser effect of sulfate of potash. Plots 17 and 18 differed a little, but the two methods do not agree in the relative positions of the two.

Mr. C. P. Jones determined the residual carbonate of lime in four of the samples, using MacIntire's method (3, p. 83-97) for determining CO₂. Plot 11 contained more carbonate than 12, while plot 15 contained less than 16. Therefore no deduction can be drawn from these studies of the lime requirements or residual carbonates that would favor either potash salt.

The results of these different methods of soil analysis show no evidence of cumulative effects or residues due to the continuous use for 22 years of two distinctly different potash salts, with the possible exception of the slightly greater retention of calcium on the muriate plots.

TABLE 3
Lime requirement of soils of field B, expressed in parts per million of dry soil

	TREATED WITH MURIATE			TREATED WITH SULFATE		
	Plot 11	Plot 15	Plot 17	Plot 12	Plot 16	Plot 18
Hopkins method.....	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.
Hopkins method.....	50.0	62.5	50.0	50.0	37.5	75.0
Veitch method.....	5712.0	5712.0	6120.0	5712.0	5314.0	5712.0

TABLE 4
Residual calcium carbonate in soils of field B, expressed in pounds per acre foot

TREATED WITH MURIATE		TREATED WITH SULFATE	
Plot 11	Plot 15	Plot 12	Plot 16
lbs.	lbs.	lbs.	lbs.
1566	1236	1170	1688

Having found but little evidence of cumulative differences in the respective effects of long continued yearly applications of muriate and sulfate of potash, some studies have been made to ascertain possible temporary differences that may arise following their application in the spring.

In this connection, a percolation experiment by the author assisted by Mr. R. W. Ruprecht, will be presented. The experiment was made in connection with other soil studies but is of use here. Samples of soil were obtained in July, 1914, from plots 11 and 12, on which, at the time, a crop of alfalfa was growing. The samples were obtained by driving cylinders of galvanized iron, 3 inches in diameter, vertically downward into the soil to a depth of 8 inches. The cylinders and contents were removed intact and taken to the laboratory. A perforated cap was placed over the bottom of each cylinder, which was then set in a vertical position over a beaker. Water

was applied to the top of the cylinder from time to time and allowed to percolate through into the beaker. The object of the experiment was to learn the nature of the substances in the drainage-water from these two plots.

One pair of cylinders was subjected to two percolations of 500 cc. each. A second pair underwent six percolations of 500 cc. each. A third pair was first saturated with water and allowed to stand 24 hours before adding more, after which it was subjected to five percolations of 500 cc. each. Each 500 cc.

TABLE 5

Composition of percolates from soils of field B, expressed in parts per million of solution

	TOTAL SOLIDS IN SUCCESSIVE PERCOLATES					
	1 p.p.m.	2 p.p.m.	3 p.p.m.	4 p.p.m.	5 p.p.m.	6 p.p.m.

Experiment 1 (air-dry soil)

Muriate soil.....	526	152				
Sulfate soil.....	270	172				

Experiment 2 (air-dry soil)

Muriate soil.....	442	114	100	92	92	98
Sulfate soil.....	246	174	124	38	80	80

Experiment 3 (core first saturated for 24 hours)

Muriate soil.....	138	80	100	72	60	
Sulfate soil.....	320	138	110	104	62	

AVERAGE COMPOSITION OF ALL PERCOLATES

	Total solids	CaO	Cl	SO ₃	Na ₂ O
	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.
Muriate soil.....	159	26	18	18	20
Sulfate soil.....	151	37	3	40	20

of water on the surface of the cylinder was equal to a depth of 4.4 inches and therefore was equal to that depth of rainfall.

Total solids were determined in each 500 cc. of percolate. Determinations of CaO, Cl, SO₃ and Na₂O were made in the combined percolates from the respective plots, after concentration to a small volume.

The total solids in the percolates decreased sharply after the first portion had passed, which is the usual result in such experiments. In experiment 3, the increased solubility of the sulfate soil over that of the muriate soil, which

is striking, may be due to the previous saturation for 24 hours; but it may also be due to the places on the plots from which the samples came. These lots of soil were not composite samples from their respective plots, but were small cores removed bodily and unmixed with other similar cores.

Only a trace of potassium could be found in the percolates. Chlorine and sulfuric acid varied as would be expected in accordance with the potash salt used. Sodium did not vary between the two plots, but calcium was notably less concentrated in the percolates from the muriate soil. This may be attributed to its greater solubility as calcium chloride and early removal after application of the fertilizer; but it also ties up with the higher amount of calcium obtained from the muriate soil in weak HNO_3 , and by fusion.

An absorption study was made with the assistance of Mr. Beals in the winter of 1916, to learn what the immediate effects were of solutions of potassium chloride and potassium sulfate respectively, on the two soils of field B. The soils were from the two series of plots, 11, 15 and 17 forming the muriate samples, and 12, 16 and 18, the sulfate samples. The soil samples were those already mentioned as secured in November, 1915.

Two hundred grams of the muriate soil were allowed to stand in contact with 1000 cc. 0.1 N KCl in a large flask, for 48 hours, while 200 gms. of the sulfate soil were in contact with 1000 cc. 0.1 N K_2SO_4 . During working hours, the mixtures were frequently shaken, and at the end of the period, the solutions were filtered and analyzed. The period of time was too short to produce equilibrium; but it should show the direction of the reaction between the potassium salts and the soils.

Potassium was absorbed more freely from the KCl than from the K_2SO_4 . A little of the Cl was retained by the soil, probably by adsorption of unchanged KCl; but from the sulfate soil there was actually extracted SO_4^{2-} in addition to that contained as K_2SO_4 .

Less Ca was removed by the KCl, which instead appeared to exchange places with Na, since there was much more sodium in the chloride solution than in the sulfate solution.

Al, Fe and Mn were found in traces in the solutions. This removal of sodium instead of calcium by the chloride solution is in harmony with the differences observed between the calcium results in the other studies.

The experiments were repeated in full, so that results were obtained on the six individual samples in duplicate. Absorption experiments are difficult to execute with closely parallel results, since the phenomena are both physical and chemical and invariable conditions are nearly impossible to maintain. The results all deviated in the same direction however, and the averages given in the table undoubtedly show the relative behavior of the two solutions on their respective soils.

Water extracts were made from each of the 1915 soil samples by shaking 50 gms. of soil with 500 cc. of water. The shaking was done at short intervals during an hour, and then the mixture was filtered through a small paper

fitted into a 3-inch funnel. The paper and a portion of the funnel were at once filled with the soil, and the filtrate was refiltered through the mass until clear. Thus the solution was practically a filtrate through soil supported by a small paper that was soon saturated with absorbed salts.

Portions of the extracts were concentrated in platinum dishes, after the addition of a few drops of phenolphthalein. The extracts from 11, 12, 15 and 16 turned pink when the volume had been condensed to less than one-fourth, while that from 17 turned just before dryness and the extract from 18 failed to change. In this qualitative comparison the extracts from the muriate soils were slightly ahead of those from the sulfate soils in reaching alkalinity. The effect on the indicator during concentration is doubtless due to the hydrolysis of calcium bicarbonate or calcium silicate.

Samples from the same plots taken one year later, in November, 1916, were extracted with water in the manner just described. Concentration of

TABLE 6
Absorption experiments with soils of field B

Muriate soils treated with 0.1 N KCl, sulfate soils with 0.1 N K₂SO₄. Absorption and extraction in milligrams per 100 grams soil

	MURIATE SOIL	SULFATE SOIL
	mgm.	mgm.
K absorbed.....	204	161
Cl absorbed.....	19	...
SO ₄ extracted.....	...	103
Ca extracted.....	47	55
Mg extracted.....	6	8
Na extracted.....	169	55

Traces of Al and Fe in all solutions. Trace of Mn found in but one solution from Plot 18.

portions of these extracts were made in platinum dishes, after addition of rosolic acid as an indicator. The extracts from 11 and 12 quickly turned to the neutral tint of this indicator but failed to show any alkalinity on further evaporation to dryness. The extracts from 17 and 18 retained the yellow or acid tint of the indicator throughout the operation. Apparently in the intervening year, the residual calcium carbonate had disappeared from these soils. Extracts were not prepared from plots 15 and 16.

The hydrogen-ion concentration was measured colorimetrically in these four extracts. The pH values were between 6.2 and 6.4, and the tints of the muriate solutions matched those of the corresponding sulfate solutions.

SUMMARY AND CONCLUSIONS

Soil from three plots treated for 22 years with muriate of potash, has been compared in its chemical behavior with soil from 3 adjacent plots treated during the same time with sulfate of potash.

Analyses of these soils showed slightly more lime in the muriate series when determined by fusion and by 0.2 *N* HNO₃. All other results were practically alike in both soils.

Percolation experiments with columns of soil taken directly from the plots, yielded slightly more total solids from the muriate series, while the sulfate series gave the higher lime. A tenth-normal solution of K₂SO₄ dissolved more Ca from the air-dry sulfate soils than a similar solution of KCl removed from the muriate soils. The KCl solution removed more Na than Ca.

The reactions of water-solutions of the soils were very slightly acid, and least in those from the muriate soils.

It is concluded that the long continued use of the two potash salts produced no important cumulative differences in the chemical properties of this soil, and that muriate of potash is no more and possibly less exhaustive of lime in the soil than sulfate of potash.

REFERENCES

- (1) Association of Official Agricultural Chemists. 1912 Methods of analysis. U. S. Dept. Agr. Bur. Chem. Bul. 107 (revised).
- (2) HULETT, G. A., AND ALLEN, L. E. 1902 The solubility of gypsum. *In* Jour. Amer. Chem. Soc., v. 24, p. 667-679.
- (3) MACINTIRE, W. H., AND WILLIS, L. G. 1913 Soil carbonates. A new method of determination. Tenn. Agr. Exp. Sta. Bul. 100.
- (4) VEITCH, F. P. 1904 Comparison of methods for the estimation of Soil acidity. *In* Jour. Amer. Chem. Soc., v. 26, p. 637-662.
- (5) WHITNEY, M. 1909 Soils of the United States. U. S. Dept. Agr. Bur. Soils, Bul. 55.

THE INFLUENCE OF THE NITROGEN TREATMENT ON THE CONTENT OF NITROGEN, CARBON AND PHOSPHORIC ACID IN A SOIL VARYING IN MECHANICAL COMPOSITION¹

A. W. BLAIR AND A. L. PRINCE

New Jersey Agricultural Experiment Stations

Received for publication June 21, 1923

The soil under observation was cropped for 10 years in cylinders of the type used at this station, in carrying out a study of the influence of the mechanical composition of the soil on the availability of nitrogen in nitrate of soda and dried blood (2).

The soil is a loam belonging to the Penn series and was modified for this work by introducing varying percentages of a rather coarse sand. Thus in addition to the loam soil alone, there were mixtures of this containing 10, 20, 30 etc. up to 100 per cent of sand (the 60 per cent sand mixture was omitted).

With the exception of 1911 when corn was grown, two crops have been grown each year for the 10 years. All of the cylinders received liberal applications of acid phosphate and muriate of potash, and lime was applied at intervals, so that acidity was not a limiting factor.

For each soil mixture two cylinders received no nitrogen, two received nitrate of soda at the rate of 320 pounds per acre and two received dried blood equivalent to the nitrate of soda. The fertilizers were applied annually to the first crop.

With the completion of the work in the fall of 1920, samples of soil were collected from all of the mixtures and these have been analyzed for total nitrogen, carbon and phosphoric acid. The analytical results are shown in table 1 along with the average yields of dry matter for the 9 years—1912 to 1920 inclusive (the figures for the corn of 1911 are included but are omitted from the averages).

A study of these figures shows that the yields from the check cylinders (no nitrogen) are much lower than those from cylinders where nitrate of soda and dried blood were used. In a number of cases the latter were more than twice as large as the former. This is shown by the final averages. The 9 year average of all check cylinders was 57.6 gm.; of all nitrate of soda cylinders 132.6 gm., and of all dried blood cylinders 120 gm. The highest average yield for the nitrate of soda cylinder was on the 10 per cent sand series. Up to 30 per cent sand the decrease in yield was slight. From this point on, there is, with one exception, a gradual decline in yield.

¹ Paper No. 135 of the Journal Series New Jersey Agricultural Experiment Stations, Department of Soil Chemistry and Bacteriology.

It is interesting to compare these figures giving the yields of dry matter, with the figures for the total nitrogen in the soil, for the three treatments at the end of the 10-year period. From an examination of the table it is at once apparent that there is very little difference between the nitrogen content of the soils that received no nitrogen during the 10 years and those that received the nitrate of soda and dried blood treatment. To take a specific case the check cylinders with 50 per cent sand show a nitrogen content of 0.0583 per cent nitrogen, whereas the corresponding nitrate of soda cylinders show 0.0608 per cent nitrogen. The difference is so slight that it is easily within the limit of error. The average yield for the nitrate cylinders however is more than twice as great as the average for the check. Furthermore,

TABLE 1

The influence of the nitrogen treatment on the yield of dry matter and the composition of the soil

SOIL MIXTURE	YIELD OF DRY MATTER, 9 YEAR AVERAGE			TOTAL NITROGEN IN SOIL AFTER 10 YEARS OF CROPPING			TOTAL CARBON IN SOIL AFTER 10 YEARS OF CROPPING			TOTAL PHOSPHORIC ACID AFTER 10 YEARS OF CROPPING		
	Check		Dried blood	Check		NaNO ₃	Check		NaNO ₃	Dried blood	Check	
	gm.	gm.	gm.	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
Loam soil....	81.4	157.0	147.9	0.1103	0.1112	0.1049	1.123	1.120	0.990	0.175	0.175	0.164
10% sand....	89.3	164.5	149.9	0.0900	0.0980	0.0964	0.958	0.853	0.993	0.155	0.154	0.167
20% sand....	70.5	152.4	135.6	0.0793	0.0848	0.0843	0.750	0.930	0.870	0.145	0.151	0.148
30% sand....	68.6	156.4	137.2	0.0673	0.0705	0.0776	0.6750	0.783	0.838	0.145	0.130	0.129
40% sand....	65.4	153.3	130.7	0.0618	0.0660	0.0681	0.8680	0.773	0.855	0.130	0.130	0.132
50% sand....	68.6	152.1	126.8	0.0583	0.0608	0.0634	0.7250	0.765	0.810	0.127	0.123	0.133
70% sand....	46.1	134.9	110.5	0.0300	0.0332	0.0382	0.3430	0.440	0.445	0.118	0.116	0.106
80% sand....	42.0	110.5	107.7	0.0240	0.0252	0.0307	0.333	0.308	0.373	0.108	0.097	0.112
90% sand....	27.9	97.8	88.3	0.0159	0.0181	0.0201	0.228	0.295	0.358	0.079	0.090	0.107
100% sand...	16.3	47.2	65.0	0.0093	0.0107	0.0093	0.215	0.195	0.150	0.073	0.075	0.054
Average....	57.6	132.6	120.0	0.0546	0.0579	0.0593	0.622	0.646	0.668	0.126	0.124	0.125

the 50-per-cent-sand cylinders gave an average yield of 152.1 gm. of dry matter as against an average of 157 gm. for the loam soil, notwithstanding the fact that the latter contains nearly twice as much nitrogen as the former.

With the 80-per-cent-sand mixture the nitrate of soda cylinders gave an average yield of 110.5 gm. of dry matter as against an average of 42 gm. for the check cylinders, although the percentage of total nitrogen in these two soils differs by only 0.0012 per cent.

The figures for total carbon in the soil are quite parallel to those for total nitrogen. Here again the differences between the percentage of carbon in the check cylinders and the nitrate of soda cylinders falls within the limit of error. It may be pointed out that roughly speaking, up to and including

the 70-per-cent-sand mixture, there is about 10 times as much carbon in these soils as there is nitrogen.

It is of interest to note that the average percentage of nitrogen and carbon for all the soil mixtures is slightly higher with dried blood than with nitrate of soda, whereas the figures for the average yields of dry matter are just the reverse.

Here then is a series of soil mixtures a part of which have received for 10 years nitrogenous fertilizers equivalent to 320 pounds of nitrate of soda per acre and others which have received no nitrogenous treatment during this period, and at the close of the period the difference between the total nitrogen and carbon content of the treated and untreated soils is very slight. At the same time the nitrogen treated soils have yielded on an average more than twice as much crop substance as the untreated soils. The fact that there has been no appreciable increase in the nitrogen content of the soils that have received the nitrogen fertilizers, over those that have received no nitrogen for 10 years, would lead one to conclude that the applied nitrogen has constituted a "revolving fund" which was being drawn upon to the full extent, by the crops and by the forces which either destroy nitrogen compounds or cause them to leach away. In other words, under the cropping system used there could be no appreciable accumulation in the soil of the applied nitrogen. The averages do indicate a very slight tendency towards accumulation, but this may be an apparent rather than a real difference.

If there remains any doubt in the mind of anyone as to the failure of a chemical analysis of the soil, taken alone, to determine its crop-producing power, certainly these figures should dispel such doubt.

It is quite evident from these results that a soil which is low in total nitrogen may be quite productive if the supply of available nitrogen is well maintained during the growing period. On the other hand a soil may show a high percentage of total nitrogen while at the same time it produces low yields, due to a deficiency of available nitrogen.

The work bears out, in a striking manner, the conclusion which Hilgard (1) reached nearly 20 years ago, namely, "The impossibility of judging correctly of a soil's productiveness from the percentage of chemical ingredients alone."

A soil of the character of the 40 or 50 per cent sand mixture, having a low percentage of total nitrogen, may give good yields if available nitrogen is applied at the right time. However, it does not follow that this is an economical method of getting good yields. It frequently pays to "build up" the total nitrogen, so that there may be a larger natural supply of available nitrogen; but this, it must be remembered, is a slow process, especially in the case of sandy soils where bacterial decomposition goes on rapidly. It is under such conditions that careful attention must be given to the "revolving" supply, that is the available nitrogen.

Russell (3) has pointed out that so far as our present knowledge goes it is impossible to maintain a high content of nitrogen on cultivated land except

at a wasteful expenditure of nitrogenous manure. In another place Russell (4) expresses the thought that the yield of crops under British conditions was perhaps more limited by the amount of nitrate present than by any other single factor.

Apparently the nitrogen treatment has had no influence on the phosphoric acid content of the soil. In practically every case, for a given soil mixture, the percentage of phosphoric acid is essentially the same for the three treatments. The average percentage of phosphoric acid for all the mixtures that received no nitrogen (check) is 0.126 per cent; the average for those that received nitrate of soda is 0.124 per cent and for those that received dried blood 0.125 per cent.

In this connection it will be remembered that the phosphoric acid treatment was uniform for all cylinders and since the nitrate of soda and dried blood cylinders yielded larger crops than the check cylinders, it necessarily follows that the crops from the former removed more phosphoric acid than the crops from the latter. Since the analysis shows that there was no essential difference in the phosphoric acid content of the soils at the end of the 10 year period, it seems reasonable to conclude that the check cylinders have lost more phosphoric acid through leaching than the nitrogen treated cylinders. This is what we should expect. With diminished crops there is greater opportunity for loss through leaching. The smaller the root system the less the amount of organic matter to catch and hold dissolved mineral matter.

SUMMARY

For a period of 10 years equivalent amounts of nitrogen in the form of nitrate of soda and dried blood were compared in cylinder experiments on a soil varying in mechanical composition, from a loam to a coarse sand.

With the exception of the first year, two crops were grown each year, the fertilizer in every case being applied for the first crop.

The 9-year average yields of dry matter are reported for the check treatment (no nitrogen), nitrate of soda treatment and dried blood treatment.

These yields are compared with the percentage of nitrogen, carbon and phosphoric acid, in the various soil mixtures, at the end of the ten years.

Attention is called to the wide difference in the yields of dry matter on the check cylinders as compared with the nitrogen treated cylinders, and the slight difference in the percentage of nitrogen and carbon in the soils from the cylinders receiving the three different treatments.

The work emphasizes very strongly the importance of available nitrogen as distinct from total nitrogen, and likewise the failure of the determination of the chemical ingredients of a soil in forecasting the productiveness of that soil.

The phosphoric acid content is essentially the same in the soils without nitrogen treatment as in those which received the nitrate of soda and dried blood treatments.

There is indirect evidence that the check cylinders lost more phosphoric acid through leaching than the nitrogen treated cylinders.

REFERENCES

- (1) HILGARD, E. W. 1906 Soils, p. 351. Macmillan Company, New York.
- (2) LIPMAN, J. G., AND BLAIR, A. W. 1921 The influence of the mechanical composition of the soil on the availability of nitrate of soda and dried blood—1920. N. J. Agr. Exp. Sta., 42d Ann. Rept., p. 303-316.
- (3) RUSSELL, E. J. 1917 Soil conditions and plant growth, p. 114 (1917 ed.), p. 184 (1921 ed.). Longmans Green and Company, N. Y.
- (4) RUSSELL, SIR JOHN 1923 Discussion of microorganisms and their application to industry and research. *In* Jour. Soc. Chem. Indus.-trans., v. 42, no. 17, p. 173-175.

EFFECT OF DRYING AND STORAGE UPON THE HYDROGEN-ION CONCENTRATION OF SOIL SAMPLES¹

CLAYTON O. ROST AND ERNEST A. FIEGER

University of Minnesota

Received for publication June 26, 1923

INTRODUCTION

The data hitherto published would indicate that the practice of using air-dry soil samples for hydrogen-ion determinations is satisfactory, especially if these are acid. Our studies lead us to conclude, however, that the only reliable indication of conditions existing in the field are obtained when hydrogen-ion determinations are made with soils samples taken freshly from the field.

Burgess (2) working with Miami silt loam from a series of plots at the Rhode Island Station found that both air-drying and oven-drying had little or no effect upon the pH values of acid soils but that drying alkaline soils rendered them somewhat less alkaline. Arrhenius (1), reporting the effect of drying on the hydrogen-ion concentration of one alkaline soil, found that neither air-drying nor drying by heat at 100°C. and 150°C. brought about any change in pH values as determined by the indicator method.

Preliminary determinations showed that some of the Minnesota soils with which we were working changed considerably in pH values upon becoming air-dry. Later we have made determinations on many of our samples both while still fresh and moist from the field and again after allowing them to become air-dry. With a small number we have studied the effect of oven-drying at 110°C. of moistening with distilled water after air-drying, and of storage in moist condition in air-tight glass containers. The effect of drying upon the indication of acidity as shown by the qualitative potassium thiocyanate method was also tested.

The hydrogen-ion concentration determinations were made by the gas chain electrometric method, using a modification of Knight's electrode vessel (3) with bubbling hydrogen and constant mechanical shaking. Double electrodes inserted in the vessel afforded an opportunity for checking the correctness of each determination. The electrodes were checked against a standard soil at the beginning of each run and all potentiometer readings were calculated to 25°C.

¹ Published with the approval of the Director as Paper No. 388, of the Journal Series of the Minnesota Agricultural Experiment Station.

EFFECT OF AIR-DRYING

The effect of air-drying upon samples taken from the same field but from plots having different lime or marl treatment is shown in table 1. The fields from which these samples were taken are some upon which liming experiments are in progress. The soils of these fields range in texture from silty clay loam to loamy sand. Where the samples became less acid on drying the difference is indicated by a minus (-) sign.

In the case of fields A and B the difference in hydrogen-ion concentration between moist and air-dry soil is not great nor is the difference between individual samples marked. The samples from field C showed a slightly greater difference but not a marked variation from the average, while those from fields

TABLE 1

Hydrogen-ion concentration of fresh and air-dry soil samples from five experimental fields

SAMPLE NUM- BER	FIELD A, SILT LOAM (WATER-LAI)			FIELD B, SILTY CLAY LOAM (GLACIAL)			FIELD C, SILT LOAM (LOESSIAL)			FIELD D, LOAMY SAND (GLACIAL OUTWASH)			FIELD E, SILTY CLAY LOAM (GLACIAL)		
	Fresh	Air-dry	Difference	Fresh	Air-dry	Difference	Fresh	Air-dry	Difference	Fresh	Air-dry	Difference	Fresh	Air-dry	Difference
	pH	pH	pH	pH	pH	pH	pH	pH	pH	pH	pH	pH	pH	pH	pH
1	5.75	5.61	0.14	5.78	5.74	0.04	5.58	5.24	0.34	5.50	5.79	-0.29	5.54	5.14	0.40
2	5.77	5.73	0.04	5.87	5.95	-0.08	5.71	5.36	0.35	5.83	6.32	-0.49	5.65	5.29	0.36
3	5.80	5.95	-0.15	5.88	5.83	0.05	5.88	5.48	0.40	6.29	6.39	-0.10	5.65	5.48	0.17
4	5.88	5.88	0	5.90	5.76	0.14	6.07	5.61	0.46	6.54	6.12	0.42	5.87	5.54	0.33
5	6.04	5.95	0.09	5.90	5.80	0.10	6.22	6.17	0.05	6.54	6.44	0.10	6.04	5.61	-0.43
6	6.07	5.95	0.12	6.02	5.85	0.17	6.48	6.27	0.21	7.34	7.30	0.04	6.26	5.11	1.17
7	5.99	6.19	-0.20	6.04	5.95	0.09	6.63	6.51	0.12	7.37	7.66	-0.29	6.36	5.95	0.41
8	6.05	5.97	0.08	6.19	6.07	0.12	7.51	7.13	0.38	7.54	7.56	-0.02	6.54	5.90	0.64
Average		0.07		0.08			0.29			-0.07			0.49		
Range.....		0.29		0.25			0.41			0.91			1.00		

D and E showed a wide range in the difference between moist and air-dry soil and a few instances of large differences between the two conditions of moistness. The acid samples showed as great a change on air-drying as did the alkaline ones. Some of the samples became more acid and others more alkaline on drying but most frequently they became more acid. From the data it appears that a constant difference between moist and air-dry samples cannot be assumed for any individual field without establishing this by a sufficient number of preliminary determinations.

In table 2 are reported the pH values of moist and air-dry samples of glacial and loessial soils taken from well distributed localities in Minnesota. The samples, from a depth as great as six feet, were divided into two groups, surface and subsoil, all samples taken below the surface six inches being included under the designation of subsoil. A pH value of 7.07 was taken as neutrality. The

samples were divided into groups having a difference in pH of 0.5 and ranging from 5.08 to 9.57. The glacial soils show a more marked increase in acidity upon drying than do the loessial. The greatest difference in the case of the surface soils of the glacial group occurred in those soils with original pH values 6.58 to 7.07. The samples with pH values of 6.08-6.57 and 6.58-7.07 showed more change than those of the two groups between pH 7.08 and pH 8.07. With the subsoils the changes became more marked as the soils became more alkaline. The acid soils of both the surface and subsoil groups showed considerable change upon air-drying.

TABLE 2

Hydrogen-ion concentration of fresh and air-dry glacial and loessial soil samples

RANGE IN pH VALUES	DIFFERENCE IN pH VALUES OF FRESH AND AIR-DRY LOESSIAL SOIL				DIFFERENCE IN pH VALUES OF FRESH AND AIR-DRY GLACIAL SOIL			
	Number samples tested	Minimum	Maximum	Average of all	Number samples tested	Minimum	Maximum	Average of all
<i>Surface soil</i>								
5.08-5.57	3	0.24	0.57	0.39	2	0.12	0.25	0.18
5.58-6.07	16	-0.05	0.73	0.39	14	0.11	0.64	0.36
6.08-6.57	9	0.32	1.24	0.64	3	0.56	0.86	0.74
6.58-7.07	3	0.48	0.73	0.62	1	1.05	1.05	1.05
7.08-7.57	0				2	0.65	0.66	0.66
7.58-8.07	0				1	0.74	0.74	0.74
<i>Subsoil</i>								
5.08-5.57	1	0.52	0.52	0.52	1	0.25	0.25	0.25
5.58-6.07	8	0.07	0.71	0.31	15	0.16	0.94	0.50
6.08-6.57	8	0.20	0.98	0.57	12	0.25	1.38	0.68
6.58-7.07	3	0.18	0.80	0.50	5	0.44	1.21	0.84
7.08-7.57	1	0.52	0.52	0.52	11	0.51	1.17	0.72
7.58-8.07	0				13	0.43	1.38	0.89
8.08-8.57	0				6	0.42	1.54	0.91
8.58-9.07	0				5	0.98	1.19	1.11
9.08-9.57	0				1	0.98	0.98	0.98

The loess soils showed a fairly constant change in hydrogen-ion concentration for surface soil and subsoil and for both acid and alkaline samples.

In determining the effect of air-drying upon the reaction obtained by the qualitative potassium thiocyanate method, approximately 10 gms. of soil were placed in a test tube, 10 cc. of a saturated ethyl alcohol solution of potassium thiocyanate added, the test tube stoppered and thoroughly shaken. After standing 15 minutes the color of the supernatant liquid was observed. It was found possible to distinguish five degrees of acidity which may be designated: very slight, slight, medium, strong and very strong. The reaction of both the fresh and air-dry soil was determined with 76 samples. Five, all

of which were neutral, showed no change while 71 became more acid upon air-drying. The amount of change bore no relation to the degree of acidity. Thirty-five samples changed one degree, nineteen changed two degrees, and seventeen changed three degrees.

EFFECT OF OVEN-DRYING

The effect of oven-drying upon the hydrogen-ion concentration as compared with air-drying is shown in table 3. For all the samples tried over-drying rendered both acid and alkaline soils more acid than when fresh and in all but four cases more acid than when air-dry. This effect was more pronounced with the samples of loess and sandy soil from glacial outwash, than with the glacial soils.

TABLE 3

Hydrogen-ion concentration of fresh, air-dried and oven-dried soil samples

SAMPLE NUMBER	GLACIAL			GLACIAL OUTWASH			LOESSIAL		
	Fresh	Air-dry	Oven-dry	Fresh	Air-dry	Oven-dry	Fresh	Air-dry	Oven-dry
1	5.60	5.58	5.04	6.32	5.33	5.21	5.85	5.63	4.60
2	6.12	5.90	5.75	6.37	5.75	5.55	5.87	5.80	5.33
3	6.20	5.90	5.55	6.78	6.34	6.18	5.90	5.75	5.16
4	7.30	6.64	7.13	6.96	6.22	5.98	5.97	5.70	4.92
5	8.00	7.39	7.79	7.00	6.39	6.17	6.32	5.90	5.19
6	8.40	7.96	8.00	7.11	6.48	6.26	6.46	6.26	5.99
7	8.79	8.34	8.30	7.20	6.54	6.04	6.63	6.12	5.34

EFFECT OF MOISTENING AIR-DRY SAMPLES

In order to determine whether samples would return to their original hydrogen-ion concentrations and in what measure if moistened after air-drying and allowed to temper, a set of the air-dry samples was moistened with distilled water and placed in air-tight glass containers. The hydrogen-ion concentrations were determined at the end of 1, 3, 23, 40 and 60 days and are reported in table 4. At the end of 1 and 3 days the two samples tested were still more acid than the original moist samples and all were set aside for 20 days. At the end of this time all were decidedly more acid than the air-dry samples with the exception of no. 7 and at the end of 40 and 60 days there was little further change. Thus it appears that soils which have become air-dry when remoistened and allowed to temper have a hydrogen-ion concentration no more nearly correct than the air-dry samples.

EFFECT OF STORAGE IN MOIST CONDITION

The effect of storage of fresh moist soils in air-tight containers on the hydrogen-ion concentration is shown in table 5. The change in pH values

varies from 0.02 to 0.64 with a range of 1.24 (-0.64 to +0.60). There is no relation in this case between the degree of acidity or alkalinity and the ultimate reaction. It would appear that soils kept in storage in this manner for any length of time are no more valuable than if they were allowed to become air-dry.

TABLE 4
Hydrogen-ion concentration of fresh, air-dried and remoistened soil samples

SAMPLE NUMBER	FRESH	AIR-DRY	REMOISTENED AND TEMPERED:				
			1 day	3 days	23 days	40 days	60 days
1	5.44	5.19	5.26	5.33	5.28
2	5.60	5.46	5.07	5.09	5.04
3	6.07	5.82	5.34	5.38	5.29
4	6.14	5.92	5.38	5.39	5.31
5	6.20	5.90	5.55	5.50	5.50
6	6.32	5.90	6.15	5.90	5.12	5.09	5.02
7	7.19	6.54	6.93	6.92	6.14	6.09	6.15

TABLE 5
Hydrogen-ion concentration of fresh and stored samples of soil

SAMPLE NUMBER	FRESH	AFTER 3 MONTHS	DIFFERENCE	SAMPLE NUMBER	FRESH	AFTER 3 MONTHS	DIFFERENCE
1	5.36	4.97	+0.39	11	6.27	5.95	+0.32
2	5.56	5.63	-0.07	12	6.27	6.05	+0.22
3	5.61	5.53	+0.08	13	6.48	6.37	+0.11
4	5.71	5.51	+0.20	14	6.54	7.10	-0.64
5	5.75	5.31	+0.44	15	6.54	6.07	+0.47
6	5.90	6.54	-0.64	16	6.66	6.64	+0.02
7	6.00	5.87	+0.13	17	6.91	6.83	+0.08
8	6.04	5.64	+0.40	18	7.51	7.22	+0.29
9	6.22	6.15	+0.07	19	7.96	7.52	+0.44
10	6.26	5.66	+0.60	20	8.05	7.56	-0.49

SUMMARY

The effect of air-drying and oven-drying upon the hydrogen-ion concentration of soil samples was determined as was also the effect of moistening and tempering samples of soil which had become air-dry and of storing the fresh moist samples in air-tight containers. The effect of air-drying upon the reaction of soil samples was tested also by the qualitative potassium thiocyanate method.

Soil samples from five fields upon which liming experiments are in progress showed differences in the pH values between the fresh and air-dry samples varying from pH 0.03 to pH 1.17. With two fields the differences were small; with two others, large; and with one, intermediate. The acid samples showed

as great a change upon air-drying as did the alkaline ones. Some samples became more acid and some more alkaline upon air-drying but the general tendency was to become more acid.

Of 144 glacial and loessial soils tested in the fresh and air-dry condition all except one became more acid upon air-drying. With the glacial subsoils the difference between the fresh and air-dry samples tended to increase as the pH increased. The maximum difference, pH 1.11, was found with the group having pH values of 8.58 to 9.07. The loess subsoils did not show this tendency. The glacial soils, in general, showed a more marked change from air-drying than the loess.

Permitting soil samples to become air-dry in most cases increased the intensity of the reaction obtained by the qualitative potassium thiocyanate method. Of the 76 samples tested, 5 showed no change, 35 a change of one degree of acidity, 19 a change of 2 degrees and 17 a change of 3 degrees.

Oven-drying rendered all soil samples tested more acid than in the fresh condition. Of twenty-one samples tested all except four were more acid than when in the air-dry condition.

Samples air-dried, then moistened with distilled water and tempered were more acid than the same soils in fresh condition. Of the seven samples tried all but one were found more acid than when in the air-dry condition.

The hydrogen-ion concentration of fresh moist soils stored for three months in air-tight glass containers changed in most cases, some samples becoming more acid and some less so, with a general tendency to become more acid. The amount of change is not related to the degree of acidity or alkalinity.

From the data reported it is concluded that the only reliable indication of conditions existing in the field are obtained when hydrogen-ion concentration determinations are made with soil samples freshly taken.

REFERENCES

- (1) ARRHENIUS, O. 1922 The potential acidity of soils. *In Soil Sci.*, v. 14, p. 223-32.
- (2) BURGESS, P. S. 1922 The hydrogen-ion concentration of soils as affected by drying. *In Science*, 55, N. S., p. 647-8.
- (3) KNIGHT, H. G. 1920 Acidity and acidimetry of soils. II. Investigation of acid soils by means of the hydrogen electrode. *In Jour. Indus. and Engin. Chem.*, v. 12, p. 457-64.

EFFECT OF SULFUR, CALCIUM AND PHOSPHORUS ON THE YIELD AND COMPOSITION OF ALFALFA ON SIX TYPES OF IDAHO SOILS¹

RAY E. NEIDIG, G. R. McDOLE, AND H. P. MAGNUSON

Idaho State Experiment Station

Received for publication March 1, 1923

Recent investigations have indicated that many soils are apparently deficient in sulfur. Some soils have shown greatly increased alfalfa yields with applications of calcium sulfate; others, with elemental sulfur. In the case of gypsum the increased yields have been attributed to sulfur, lime, or in some cases to a stimulating effect on the soil itself. Much data on record seem to show that gypsum has increased the amount of soluble plant-food in the soil extract (chiefly potassium) while on the other hand an equal amount of data can be found which controverts this view. When all data are reviewed, one arrives at the conclusion that both views are in a measure correct, for there is no doubt that different soil types respond differently to applications of gypsum. The real effect of gypsum and calcium carbonate on soils is aptly expressed by Lipman and Gericke (6). They state "All soils do not behave alike when treated with CaSO_4 or CaCO_3 . They should not be expected to do so considering their mineral composition, the law of chemical equilibrium, and the nature of colloid action in soils."

This work was started on six of the principal soil types of the state in order to determine their need, if such existed, for certain fertilizers and amendments. The soils used in this experiment are Moscow loam, Helmer silt loam, Sandpoint soil, Aberdeen soil, Boise silt loam and Palouse silt loam. They are described as follows:

Moscow loam. The sample used in this experiment was obtained from an area southeast of Moscow which was shown to be well within the area mapped under that series in the Latah County Soil Survey (1). The Moscow series is described therein as a residual soil "the surface of which is of light brown to brown in color, with light grayish brown to yellowish brown variations. They overlie subsoils of grayish yellow or yellowish brown to pale yellow color." The deeper subsoils frequently consist of disintegrated rock and grade into a substratum of bed rock. The soils of this series are developed from weathering of granites, schists, gneisses or quartzites though influenced in some localities by admixtures of fine grained loessial or windlaid material." The sample was taken from a field that had been in wheat for several years.

¹ The work presented in this paper was carried out as a coöperative project between the departments of agricultural chemistry and agronomy.

Helmer silt loam. "The soils of the Helmer series (1) are pale yellow to yellow in color with light grayish-yellow to brownish-yellow variations. The upper subsoils are usually of slightly lighter yellow to grayish-yellow color; the deeper subsoils are similar or slightly darker in color and usually compact, the structure in places approaching a hard pan in densely forested areas. The surface material under dry field conditions sometimes assumes a light grayish or bleached appearance, this being most noticeable on slopes where the grayish compact subsoil has been exposed. The Helmer soils are low in organic matter. They are derived from aeolian deposits and the soil and subsoil material is non-calcareous. The topography is gently rolling to undulating and drainage is well developed. The areas under cultivation have been cleared of timber and much of the series is still in forest." The sample used in these experiments was taken from a field that had been under cultivation for a number of years.

Sandpoint soil. The sample obtained from the Sandpoint Substation is not included in any of the soil maps of Idaho. The soil is characteristic of the timbered areas of the northern portion of this state having supported a heavy growth of white pine and other coniferous trees. In texture this soil would be classed as silt loam. The surface soil is yellow to yellowish-brown in color and is characterized by a lack of lime. The subsoils are lighter in color, in places very fine in texture approaching a shale. The subsoil varies in different parts of the area and is usually well supplied with lime, especially below the third foot.

The area from which this sample was taken is included in the Purcell Trench which extends from the southern end of Lake Coeur d'Alene to the 49th parallel. The soils have been formed from materials deposited under lacustrine conditions existing subsequent to the glacial period. The sample used came from a freshly cleared field which was being prepared for the first crop.

Aberdeen soil. The sample obtained from the Aberdeen substation is not included in any of the soil maps of Idaho. These soils are of mixed origin having been formed from the disintegration of the underlying basalt together with windblown material carried into the region. The surface is a yellowish-buff of fine sandy loam underlaid by a subsoil of very similar material to a depth of three feet or more. The subsoil contains streaks of sand from two to six inches in thickness found at a depth of 3 feet or more. This soil originally supported a growth of sage brush and other desert vegetation. The field from which the sample was taken had grown several crops of alfalfa and small grains.

Boise silt loam. The sample of soil taken from the Caldwell Substation farm near Caldwell is mapped (5) by the Bureau of Soils as Boise sandy loam. This type was later changed to Boise silt loam. The particular sample used in this work is a very fine sandy loam. It is described as "a grayish colored light sandy loam with a soft, ashy feel carrying a large amount of silt and having an average depth of about 2 feet. The subsoil of this type south of the Boise River is a loam or clay loam which has an average depth of about 18 to 24 inches. This is underlain by a sandy loam, sand or gravel cemented together into calcium carbonate to form a hardpan." The sample used came from a field that had been under cultivation for several years. A rotation including alfalfa, corn and small grains had been practiced.

Palouse silt loam. The sample of Palouse silt loam soil was taken from one of the fields on the University farm. This soil is described (1) as follows: "The soil of the Palouse silt loam to a depth of 8 to 14 inches is a dull brown or dark brown silt loam, underlain to a depth of 36 to 40 inches by a brownish-yellow to brown or light brown silt loam or silty clay loam, which usually grades into a silty clay or a silty clay loam in the lower subsoil. The lower subsoil is usually yellowish-brown or brownish-yellow, lighter in color than the intermediate and rests upon a tawny-yellow substratum of homogeneous and unstratified loessial deposit of fine texture from which the soil material is derived. This rests upon underlying bedrock at depths ranging from a few feet to 50 feet or more. The surface soil is high in organic matter and when wet is nearly black in color. The brown tint is more pronounced under dry field conditions." The sample used consisted of the surface 8 inches taken from a field in which a rotation including peas, corn and wheat had been followed with a dressing of manure every second or third year.

The moisture equivalent of each of the soil types used in this experiment were determined by the method of Briggs and McLane (3). The total sulfur content of each soil was determined by the sulfur bomb method (7) and expressed as percentage of anhydrous soil. These results are given in table 1.

TABLE 1
Total sulphur and moisture equivalents of soils

SOIL TYPE	TOTAL SULFUR CONTENT	MOISTURE EQUIVALENT	
		per cent	per cent
Moscow loam.....	0.007	25.0	
Helmer silt loam.....	0.008	24.9	
Sandpoint.....	0.016	39.7	
Aberdeen.....	0.017	17.9	
Boise silt loam.....	0.019	20.4	
Palouse silt loam.....	0.023	26.1	

PLAN OF EXPERIMENT

Three-gallon stone jars were filled with soil and treated with fertilizers and amendments at the following rates per acre:

- | | |
|-------------------------------------|---|
| 1. 2000 pounds lime | 6. 500 pounds sulfur (to all soils except |
| 2. 2000 pounds lime, 100 pounds | Moscow loam and Aberdeen) |
| sulfur | |
| 3. 100 pounds sulfur | 7. 300 pounds raw rock phosphate, (to |
| 4. 200 pounds gypsum | all soils except Moscow loam |
| 5. 200 pounds Treble Superphosphate | and Aberdeen) |

These materials were intimately mixed with the top four inches of soil. Check pots without applications of fertilizers were, of course, included in the series for each soil. The treatments were made in triplicate. Alfalfa was grown on two of the three pots while the third pot was kept in a fallowed condition. Since this was a greenhouse experiment it was possible to make seven successive cuttings which was done with all of the cropped pots except certain ones containing sandpoint soil. The cuttings were made as in common farm practice, i.e., when the new stalks began to appear.

The crop record is included in table 2 along with some data on the composition of the alfalfa. Total sulfur was determined by the regular A. O. A. C. method (2).

DISCUSSION

Moscow loam. This soil was lowest in total sulfur, containing 0.007 per cent, and closely corresponds to the Helmer silt loam which had 0.008 per cent sulfur. A slight increase in total yield of alfalfa over the check pots was obtained when 2000 pounds of lime were used. The greatest increase in yield in this series was with the combination of 2000 pounds of lime plus 100 pounds of sulfur.

TABLE 2
Yield and composition of alfalfa as affected by soil treatments

SOIL TREATMENT PER ACRE	TOTAL DRY WEIGHT OF 7 CROPS (AVERAGE OF DUPLICATES)	INCREASE OF ALFALFA OVER CHECK	TOTAL SULFUR IN CROP	TOTAL NITROGEN IN CROP	TOTAL SULFUR IN ALL CROPS	TOTAL NITROGEN IN ALL CROPS
<i>Moscow loam</i>						
No treatment.....	66.9	0.145	2.60	0.097	1.74
Lime.....	80.2	19.9	0.140	2.79	0.112	2.24
Lime and sulfur.....	125.2	87.3	0.280	3.10	0.351	3.87
Sulfur.....	97.6	45.9	0.345	3.06	0.337	2.98
Gypsum (CaSO_4).....	114.6	71.3	0.320	3.27	0.367	3.75
Treble Superphosphate.....	115.7	73.0	0.165	3.00	0.191	3.47
<i>Helmer silt loam</i>						
No treatment.....	60.4	0.140	2.60	0.084	1.57
Lime.....	54.2	-10.3	0.180	2.91	0.974	1.57
Lime and sulfur.....	118.6	96.4	0.330	3.53	0.393	4.19
Sulfur.....	132.7	119.6	0.295	3.04	0.391	4.04
Sulfur, 500 lbs.....	133.1	120.3	0.450	3.02	0.600	4.01
Gypsum.....	101.8	68.6	0.230	3.13	0.234	3.19
Treble Superphosphate.....	79.3	31.3	0.185	2.86	0.147	2.26
Raw rock phosphate.....	74.0	22.5	0.205	2.86	0.152	2.12
<i>Sandpoint</i>						
No treatment.....	91.3	0.185	2.93	0.168	2.67
Lime.....	68.4	25.1	0.190	2.85	0.130	1.95
Lime and sulfur.....	116.7	27.8	0.290	3.12	0.339	3.64
Gypsum.....	125.4	37.3	0.285	3.24	0.357	4.06
No treatment.....	51.7*	0.230	3.37	0.118	1.74
Sulfur.....	69.7*	34.8	0.390	3.70	0.272	2.57
Sulfur, 500 lbs.....	76.7*	48.8	0.475	3.51	0.364	2.69
Treble Superphosphate.....	54.8*	6.0	0.250	3.38	0.137	1.86
Raw rock phosphate.....	56.1*	8.5	0.250	3.37	0.140	1.89
<i>Aberdeen</i>						
No treatment.....	56.4	0.300	3.02	0.169	1.70
Lime.....	62.2	10.3	0.340	2.79	0.211	1.73
Lime and sulfur.....	59.5	5.5	0.390	2.97	0.231	1.77
Sulfur.....	74.5	32.1	0.395	2.97	0.294	2.21
Gypsum.....	65.5	16.1	0.370	3.06	0.242	2.00
Treble Superphosphate.....	98.4	74.4	0.210	2.94	0.206	2.89

* These totals represent four crops only.

TABLE 2—Continued

SOIL TREATMENT PER ACRE	TOTAL DRY WEIGHT OF 7 CROPS (AVERAGE OF DUPLICATES)	INCREASE OF ALFALFA OVER CHECK	TOTAL SULFUR IN CROP	TOTAL NITROGEN IN CROP	TOTAL SULFUR IN ALL CROPS	TOTAL NITROGEN IN ALL CROPS
<i>Boise silt loam</i>						
No treatment.....	81.2	0.275	3.23	0.223	2.62
Lime.....	90.5	11.5	0.305	3.08	0.276	2.78
Lime and sulfur.....	79.8	-1.7	0.315	3.09	0.251	2.47
Sulfur.....	78.4	-3.4	0.435	3.15	0.341	2.47
Sulfur, 500 lbs.....	77.9	-4.1	0.460	3.37	0.358	2.62
Gypsum.....	82.4	1.5	0.440	3.12	0.362	2.56
Treble Superphosphate.....	101.9	25.5	0.340	3.34	0.346	3.40
Raw rock phosphate.....	79.9	-1.6	0.330	3.33	0.263	2.66
<i>Palouse silt loam</i>						
No treatment.....	72.0	0.170	2.86	0.122	2.06
Lime.....	97.6	35.6	0.160	2.83	0.156	2.76
Lime and sulfur.....	151.9	110.9	0.355	3.04	0.539	4.61
Sulfur.....	137.9	91.5	0.435	2.77	0.600	3.82
Sulfur, 500 lbs.....	126.3	75.4	0.470	2.59	0.594	3.27
Gypsum.....	129.1	79.2	0.345	2.58	0.445	3.33
Treble Superphosphate.....	65.3	-9.3	0.180	2.69	0.118	1.76
Raw rock phosphate.....	70.1	-2.6	0.150	2.35	0.105	1.64

Both sulfur alone and gypsum treatments resulted in increased yields, gypsum showing the greater effect. Treble Superphosphate (200 pounds per acre) caused slightly higher yields than gypsum. This phosphate fertilizer is high in available phosphoric acid, usually containing 46-48 per cent P_2O_5 .

It is evident that lime alone did not produce an increase in sulfur content. Lime and sulfur in the combinations used in this experiment doubled the percentage of sulfur in the crop over that grown on the check. Sulfur alone caused the highest sulfur content and gypsum a sulfur content only slightly less. The application of Treble Superphosphate apparently had but little effect on the sulfur content of the crop which was in this case only slightly higher than the check.

The effect of the treatments on the nitrogen content is marked. All treatments caused an increased percentage of nitrogen in alfalfa. These increases were in the following order, reading from the lowest to the highest; check, 2000 pounds lime, 200 pounds Treble Superphosphate, 100 pounds sulfur, 2000 pounds lime and 100 pounds sulfur and 200 pounds of gypsum. When the total amount removed by crops is considered, the order is: check, lime alone, sulfur alone, Treble Superphosphate, gypsum and lime and sulfur.

Helmer silt loam. The Helmer silt loam contained 0.008 per cent sulfur. All applications except lime alone produced increased yields over the check soil, the sulfur applications producing the highest yields of all treatments. Five hundred pounds of sulfur produced a greater increase than 100 pounds. The yields with sulfur plus lime and with gypsum were still less. Both raw rock and Treble Superphosphate show an increase in yield.

All treatments increased the percentage of total sulfur in the crop, the sulfur treatments most. The application of 500 pounds of sulfur produced alfalfa containing 50 per cent more sulfur than was found in the crop grown with the 100-pound application.

All treatments increased the percentage of nitrogen in the crop. Sulfur and lime caused the highest content and highest total removed by the crop, with the 100-pound application of sulfur, the 500 pounds of sulfur, and gypsum following in the order named for total nitrogen removed.

Sandpoint soil. With some treatments on this soil only four crops were grown because of lack of soil at the time the experiments were commenced. An additional check series was used in these cases. It is interesting to note that the average of the four crops and the average of the seven crops grown on the same soil were practically identical. The sandpoint soil contains .016 per cent of sulfur. Additions of 2000 pounds of lime reduced the yield to approximately one-fourth that secured on the check. Two thousand pounds of lime plus 100 pounds of sulfur increased the yield 27.8 per cent. Sulfur alone (100 pounds) increased the yield 34.8 per cent, and 500 pounds increased it 48.4 per cent, while gypsum caused an increase of 37.3 per cent. It is seen that sulfur alone, sulfur and lime, and sulfur in the form of gypsum all materially increase the yield of alfalfa. Raw rock phosphate increased the yield 8.5 per cent, while Treble Superphosphate caused a 6 per cent increase only.

In discussing the effect of the treatment on the sulfur and nitrogen content of the alfalfa, the reader must bear in mind that there are two checks, one for the seven crop series and one for the four crop series. Lime additions show practically the same sulfur content as the check. Sulfur applications, either with or without lime, or in the form of gypsum, all caused marked increases in the sulfur content of the crop. The heavier applications produced correspondingly heavy percentages of sulfur in the alfalfa, without increasing the nitrogen content over that produced by the lighter applications of sulfur. This might be taken as an indication that the lighter application of sulfur is sufficient for the number of crops grown. All treatments of lime and sulfur, gypsum and sulfur alone increased the nitrogen content of the alfalfa over the check.

Aberdeen soil. This soil contains .017 per cent of sulfur. Lime and sulfur and 2000 pounds of lime produced only slight increases in yield. Gypsum produced a slightly better increase. Sulfur alone caused a higher yield than any of these while Treble Superphosphate caused the highest yield of all.

The effect of these treatments on the sulfur content of alfalfa is quite marked. All treatments except Treble Superphosphate caused an increase in sulfur content. Phosphates lowered the percentage considerably with this soil.

The effect on the nitrogen content is not so marked in this series. The check crop had the highest nitrogen content except for pots treated with gypsum. For all other treatments, the nitrogen content was slightly lower than the check. When the total amount removed by the crops is considered, sulfur, gypsum, and phosphate applications all show increases over the check.

Boise silt loam. This soil shows a total sulfur content of .019 per cent. The only treatment that showed a marked effect upon the yield was Treble Superphosphate. For all treatments, the crop had a higher percentage of sulfur than the check. Sulfur, gypsum, and sulfur with lime caused the greatest increases. In this series the heavier applications of sulfur resulted in higher percentages in the crop. No striking differences are noted in the effect of the treatments on the nitrogen content of the crop, except in the case of the Treble Superphosphate which resulted in an increase in nitrogen content and in the total amount of nitrogen removed by the crop.

Palouse silt loam. The Palouse silt loam had the greater sulfur content of the soils studied, viz., .023 per cent. In this series, additions of lime alone, lime and sulfur, sulfur, and gypsum all caused marked increases in yield. The greatest increase was due to one ton of lime and 100 pounds of sulfur. One hundred and five hundred pounds of sulfur gave very nearly the same results. This indicates that the application of 100 pounds of sulfur per acre is sufficient for the Palouse silt loam. Indications are that lime alone benefits alfalfa on this soil but the best yields are produced when both lime and sulfur are applied. Raw rock phosphate and Treble Superphosphate both depressed yields slightly showing that phosphates are not necessary for alfalfa on this soil.

All forms of sulfur produced a marked effect on the sulfur content of the crops. Here again the larger addition of sulfur did not materially increase the percentage of sulfur in the crop but did decrease the yield slightly in comparison with the smaller application.

No uniformity exists in the data on nitrogen content since only the lime and sulfur additions caused increases. All treatments, with the exception of the phosphates, increased the total nitrogen removed by the crop. Lime and sulfur caused the largest removal and 100 pounds of sulfur and gypsum respectively less. Five hundred pounds of sulfur produced the same result as gypsum. Phosphates show a depressing effect on the total nitrogen removed by the crops.

When the relationship of the sulfur content of the soil is compared to the sulfur content of the alfalfa grown on the soils without treatments, it is seen that the soil richest in sulfur does not produce alfalfa with the highest percentage of sulfur. The two non-treated soils producing the highest percentage of sulfur in the alfalfa are the Aberdeen soil and Boise silt loam. Both are arid soils from southern Idaho requiring irrigation before crops can be grown. Both soils contain less sulfur than the Palouse silt loam. It is thought that the Palouse silt loam, while containing the highest percentage of total sulfur, does not contain as much of the sulfur in an available form for the

plant, but rather contains a high percentage in combination with organic matter and unavailable until decomposition and oxidation take place.

Moscow loam and Helmer silt loam contain practically the same amount of sulfur and produce alfalfa with equal sulfur contents. Both soils respond to sulfur treatments in producing increased yields of alfalfa, increased percentages of sulfur in the alfalfa, and increased percentages of nitrogen. In fact the only soil which does not respond with an increase in nitrogen in the alfalfa when sulfur is applied is the Boise silt loam. All other soils show marked increases in the nitrogen content of the crop when some form of sulfur is applied. Both the southern Idaho soils, (the arid soils) appear to have sufficient sulfur for normal plant growth. It is thought that where additions of sulfur cause a slight increase in yield on these soils that there is some effect other than that of supplying the sulfur needed as a plant food. On the humid soils of northern Idaho there is not only a marked increase in yield, but a like increase in the sulfur and nitrogen content of the alfalfa grown thereon, indicating that low yields secured on the check soils are due to an actual lack of available sulfur.

THE EFFECT OF LIME, LIME AND SULFUR, GYPSUM AND SULFUR ALONE, ON THE
AMOUNT OF WATER SOLUBLE POTASSIUM IN THE DIFFERENT
SOILS

The general opinion expressed by many text books that additions of lime and gypsum to soils results in a greater amount of available potassium and other elements in the water extract has been disputed to a considerable degree in late years. These experiments were carried out to show the effect of lime, lime and sulfur, sulfur, and gypsum on the total potassium found in a water extract obtained under definite conditions for each soil. For this purpose soil was used from the control pots of the experiments just reported which had stood for more than a year in a fallowed condition. Only the potassium was considered, since this element usually showed the largest fluctuation in the water extracts from soils studied by other investigators.

Two thousand grams of soil was made up to a definite moisture content, allowed to stand twenty-four hours and then packed into a percolator. The amount of water added differed for each soil type but was the same for all treatments of the same soil. Definite amounts of distilled water were added to each soil and after the first drop of percolate appeared, the percolator was closed, for 24 hours, then opened and the first 500 centimeters collected. This was evaporated to a small volume and the potassium determined gravimetrically. The results are comparative only within a given soil series. The authors wish to state that this method is intended only to show relative differences and the results should be interpreted as such. No comparisons should be made except within the same soil types. The method was chosen because of difficulty encountered in securing uniform results on small amounts of potassium when the colorimetric method of Cameron and Failyer (4) was used. Data are given in table 3.

An inspection of table 3 shows no uniformity in the effects of the treatments on the water soluble potassium. Varying effects are noted with the same treatments on different soils. While the results are only relative, they indicate that statements frequently found in text books on the effect of calcium sulfate and calcium carbonate on the solubility of potassium in the water extract of soils are altogether too general. Our results indicate that the effects may vary with different soils, which is only to be expected when the wide differences in composition of all soils is considered.

TABLE 3
Soluble potash in soils

TREATMENT	MOSCOW LOAM	HELMER SILT LOAM	SANDPOINT SOIL	ABERDEEN SOIL	BOISE SILT LOAM	PALOUSE SILT LOAM
	gm.	gm.	gm.	gm.	gm.	gm.
None.....	0.0086	0.0109	0.0077	0.0422	0.0186	0.0120
Lime.....	0.0112	0.0050	0.0527	0.0147	0.0095
Lime and sulfur.....	0.0080	0.0068	0.0416	0.0152	0.0131
Sulfur.....	0.0115	0.0113	0.0450	0.0146	0.0151
Gypsum.....	0.0107	0.0075	0.0101	0.0500	0.0153	0.0150

SUMMARY

The effect of additions of lime, sulfur, gypsum and phosphorus on the yield of alfalfa, on the nitrogen and sulfur content of the crop, and on the soluble potash in the water extract of the soil was studied on six Idaho soils.

Four of these soils are from the humid portion of the state and two from the arid portion.

Sulfur in some form produced a distinct increase in the yield of alfalfa grown on the soils from the non-irrigated part of the state. The application of sulfur to the arid soils produced no marked effect upon the yield of alfalfa.

Sulfur in all forms produced an increase in the total nitrogen removed by the alfalfa. All applications of sulfur increased the percentage of sulfur in the plant.

Different forms of sulfur produced varied effects for each soil on the yield and composition of the crop. Phosphorous increased the yield of alfalfa on all but two of the soils. The arid soils give a greater response to applications of phosphorous and less to sulfur than humid soils. All applications of phosphorous increased the percentage of sulfur in the alfalfa and produced slight increases in the nitrogen content of the alfalfa in all but two of these soils.

The effect of these treatments on the soluble potash is variable, depending upon the soil type.

REFERENCES

- (1) AGEE, J. H., GRAVES, GEORGE W., AND MICHELWAITE, C. B. 1915 Soil Survey of Latah County, Idaho. *In* U. S. Dept. Agr., Field Operations of the Bureau of Soils, 1915, p. 2179-2197.
- (2) ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS 1919 Official and Tentative Methods of Analysis. Williams & Wilkins, Baltimore.
- (3) BRIGGS, L. G., AND McLANE, J. W. 1907 The moisture equivalent of soils. U. S. Dept. Agr., Bur. Soils, Bull. 45.
- (4) CAMERON, F. K., AND FAILYER, G. H. 1903 The determination of small amounts of potassium in aqueous solutions. *In* Jour. Amer. Chem. Soc., v. 25, p. 1063.
- (5) JENSEN, CHARLES A., AND OLSHAUSEN, B. A. 1901 Soil survey of the Boise area, Idaho. *In* U. S. Dept. Agr., Field Operations of the Bureau of Soils, 1901, p. 421-441.
- (6) LIPMAN, C. B., AND GERICKE, W. F. 1918 Does CaCO_3 or CaSO_4 treatment affect the solubility of the soils' constituents? Univ. Cal. Pub., Agr. Sci. Ser., v. 3, no. 10, p. 271-282.
- (7) OLSON, GEORGE A. 1917 The estimation of sulphur in plant material and soil. Wash. Agr. Exp. Sta. Bul. 145.

PARTIAL STERILIZATION OF SOIL, MICROBIOLOGICAL ACTIVITIES AND SOIL FERTILITY: I¹

SELMAN A. WAKSMAN AND ROBERT L. STARKEY

New Jersey Agricultural Experiment Stations

Received for publication June 25, 1923

The soil harbors a large number of microorganisms belonging to various groups which have different physiological functions. Conditions favorable to some organisms may prove injurious to others. The various bacteria, algae, fungi, actinomycetes, protozoa, nematodes, etc., carry on their activities which may or may not lead to phenomena favorable to soil fertility; some decompose organic matter with the liberation of ammonia, some use the nitrogen-free organic matter as a source of energy to fix atmospheric nitrogen, while others assimilate the ammonia using the carbohydrate as a source of energy and build up microbial proteins; still others use the ammonia as a source of energy and convert it into nitrites and then nitrates. Some organisms produce substances toxic or beneficial to others, while some actually consume others. All these various groups of organisms are united by the one common medium—the soil. As a medium the soil is affected by the content of nutrients, the condition in which these nutrients are present in the soil, the water content of the soil and transportation of salts, soil aeration, oxygen tension, carbon dioxide production, soil temperature and colloidal structure of the soil, with surface and adsorption phenomena.

When any one of these factors is changed, there is a corresponding change in the biological composition of the soil, in other words any change of the physical, physico-chemical and chemical soil condition will greatly modify the biological flora. The extent of this modification is, however, only partly known. We know, for example, that a change in soil reaction will bring about a relative change in the number of microorganisms. The same is true of soil aeration or lack of aeration. The addition of undecomposed organic matter will greatly stimulate the development of various microorganisms. Partial sterilization of the soil has been extensively studied during the last few years. This was due to the stimulus given by the excellent contributions of Russell and his associates and the hypothesis put forth on the destructive influence of protozoa upon bacteria. The limitation of the activities of soil bacteria is supposed to result in a limitation of soil fertility. According to Russell, the partial sterilization of soil by volatile antiseptics or steam brings about a

¹ Paper No. 137 of the Journal Series, New Jersey Agricultural Experiment Stations, Department of Soil Chemistry and Bacteriology.

destruction of the protozoa; this stimulates the development of bacteria and increases the fertility of the soil. This hypothesis has been criticized by different investigators who found that the favorable influence of heat and antiseptics upon the soil flora and growth of cultivated plants is due to other phenomena, like the destruction of pathogenic organisms, direct stimulation of plants, liberation of available plant-food, dissolution or redistribution of the soil fats, destruction of toxins, etc.

Without reviewing in detail the subject of partial sterilization of soil, which has been done by Kopeloff and associates (29), we may merely point out some of the facts that have been established as bearing upon the problem at hand. The purpose of the following investigations is not to disprove or to prove any fixed theory, but to throw light on the interrelationships of soil microorganisms and their activities as affected by various soil treatments, including partial sterilization.

The established facts in regard to the influence of partial sterilization upon soil biological activities may be briefly summarized as follows:

- ✓ 1. Partial sterilization of soil by heating above 60°C. or by treatment with vapors of volatile antiseptics such as toluene and carbon bisulfide, causes a fall and then a rapid rise in bacterial numbers. The resulting numbers of bacteria are far above the numbers in the untreated soil [Hiltner and Störmer (21), Russell and Hutchinson (47, 48), Fred (11, 12)].
- ✓ 2. The rise in numbers of bacteria is accompanied by an increase in the accumulation of ammonia over the untreated soil; this is formed from the decomposition of the organic nitrogen compounds in the soil [Störmer (51, 52), Russell and Hutchinson (47, 48), Scherpe (49), Fred (11, 12)].
- ✓ 3. When untreated soil is added to partially sterilized soil, there is a more rapid increase of bacterial numbers and ammonia accumulation than in the uninoculated soil. The initial rise in the former soil is followed sooner by a fall in numbers than in the uninoculated, especially in soils rich in organic matter [Russell (46), Fred (12)].
- ✓ 4. In the uninoculated soil, bacterial numbers remain at a high level for a long time [Hiltner and Störmer (21), Russell and Hutchinson (47, 48)].
- ✓ 5. There is some evidence for the assumption that the rapid bacterial development may be due to the elimination of other organisms, originally present in the soil, ("detrimental factor" according to Russell and Hutchinson) by the use of heat or antiseptics.
- ✓ 6. Protozoa, particularly the amoebae and ciliates are killed in the process of partial sterilization [Russell and Hutchinson (47, 48), Buddin (4)]. Since certain protozoa, particularly ciliates and amoebae are known to destroy bacteria in liquid cultures [see also Cutler (6)], Russell and Hutchinson assumed that the protozoa are the detrimental organisms, which keep in check bacterial development. This assumption was further substantiated by the demonstration of Cutler, Crump and Sandon (7) that an inverse relationship was found between the numbers of bacteria and active amoebae in 86 per cent of the observations made by counting these organisms on 365 consecutive days.
- ✓ 7. In addition to bacteria, other groups of soil microorganisms, particularly the fungi and actinomycetes are capable of decomposing soil organic matter with the liberation of ammonia.
- ✓ 8. Heat and volatile antiseptics have a destructive influence upon soil fungi [Bolley (2), Waget (55)].
- ✓ 9. Nothing has been said in the work of Russell and associates about the rôle of fungi in the soil. There may be hundreds of thousands of these organisms in a gram of soil, especially in soils rich in organic matter, both in the form of spores and as vegetative mycelium.

Moore (35) pointed out that, "to those that are familiar with the rapidity and certainty with which some of the fungi reduce organic to inorganic matter it is evident that there is no group of organisms present in the soil more capable of producing profound changes in its environment."

10. Fungi utilize available energy very economically, converting up to 50 per cent of the available carbon into fungous mycelium [Kruse (31)]. Since fungous mycelium contains 3 to 7 per cent of nitrogen, large quantities of nitrogen have to be assimilated in the synthesis of fungous protoplasm. Bacteria make only a limited growth in comparison with the amount of change produced, and will, therefore, convert only comparatively small amounts of nitrogen into microbial protein.

11. The actinomycetes, which form 10 to 50 per cent of the organisms developing on the plate, grow only slowly, particularly in soil treated with antiseptics [Hiltner and Störmer (21), Greig-Smith (18)].

✓ 12. The bacteria that account for the rapid rise in numbers after partial sterilization belong chiefly to the slow-growing, non-spore forming, gelatin non-liquefying bacteria [Hiltner and Störmer (21)]. There is some evidence that under certain conditions, at least, spore-bearing (butyric acid) bacteria develop rapidly [Truffaut and Bezsonoff (53)].

✗ 13. Nitrifying bacteria are destroyed or temporarily put out of action by partial sterilization, but when reintroduced they become very active [Störmer (51, 52), Russell and Hutchinson (47, 48), Fred (11, 12)].

14. Protozoa, at least most flagellates and some ciliates, can also live in organic and inorganic media [Peters (41), Aliekseiev (1)], without depending for their nutrients upon living bacteria. It is even possible that the protozoa may play a decidedly beneficial rôle in the transformation of organic and inorganic substances in the soil, as we might conclude from the results of Crabtree (5) on the protozoa in the sewage bed and Aliekseiev (1) on the protozoa in the manure pile. Protozoa may also feed on smaller protozoa and on fungous mycelium [Francé (10)], while Goodey (15) found that the addition of protozoa to a soil free from these organisms did not act as a factor limiting bacterial activities. According to Nasir (38) protozoa exert no depressing effect on nitrogen-fixing bacteria, both in sand and in solution; as a matter of fact the presence of protozoa resulted in a decided increase in nitrogen-fixation in 31 out of 36 experiments.

✓ 15. Not all the protozoa, especially the flagellates, are always destroyed by the disinfectant [Gainey (13, 14), Fred (11, 12), also Greig-Smith].

Changes in the microbial flora of the soil similar to those produced by partial sterilization will result also from other treatments of soil.

16. Air-drying of soil followed by moistening also produced a decidedly stimulating effect upon bacterial development [Rahn (44), Ritter (45)].

17. Calcium oxide produces a condition in the soil very similar to partial sterilization [Miller (34), Hutchinson (22), Hutchinson and McLennan (23)].

18. Treatment of soil with lime, antiseptics and heat makes soluble a great deal of plant food, including carbon and nitrogen compounds, as well as phosphates and other minerals. This was shown by Hutchinson and McLennan (23) for lime; by Krüger and Schneidewind (30), Kelley (25), Boyoucos (3), Wilson (59), Fischer (9), Mann, *et al.* (33), and others for heat; and by Heinze (19, 20), Pickering (42) and others for disinfectants.

19. Antiseptics and heat modify the physical condition of the soil [König, *et al.* (28), Mann, *et al.* (33), Löhnis (32)].

20. Antiseptics dissolve the soil fats [Greig-Smith (16)], thus aiding the attack upon the soil organic and inorganic matter by microorganisms.

21. Small quantities of antiseptics exert a stimulating effect upon plant growth, as shown by Koch (26, 27), Fred (11, 12) and Oldenbach (40).

22. When heated soil is treated with antiseptics, the favorable influence upon bacterial development and ammonia formation is greatly increased [Greig-Smith (16)].

23. Certain soil organisms, including fungi, actinomycetes and bacteria produce substances toxic to the growth of others [Greig-Smith (16, 17, 18), Nadson and Zolkiewicz (37)]. Antiseptics and heat lead to a neutralization of certain toxic substances present in at least some soils [Greig-Smith (16)].

24. Carbon dioxide formation in soils is also increased as a result of treatment with antiseptics and heat [van Suchtelen (54), Fischer (9)]. At first this is parallel with the increase in bacterial numbers, but the carbon dioxide production soon falls down, while the numbers are still at a high level; this was explained by Fischer as due to the fact that the bacteria pass into a condition of a low respiratory power, but still capable of developing on the plate into colonies. An increase in the amount of oxygen absorbed by the microorganisms of the soil as a result of treatment of soil by heat and volatile antiseptics has been observed by Darbshire and Russell (8).

25. The work of Hiltner and Störmer (21) as well as that of Fischer (9), Moritz and Scherpe (36) suggests that the disinfectant alters the balance of the microbial flora in the soil.

The favorable influence of volatile antiseptics and heat upon the growth of plants and microorganisms has been thus variously explained and the following theories or hypotheses have been suggested.

1. Direct stimulation. Plant roots and microorganisms may be stimulated directly by small quantities of antiseptics [Koch (26), Fred (11)].

2. Indirect stimulation of bacteria. The organic matter in the soil may be modified in such a manner as to make it more available for bacterial action; this may be due either to the removal of the fats [agriculture theory of Greig-Smith]; to greater solubility of carbohydrates, nitrogen compounds, or phosphates [Stoklasa (50)]; to the killing of worms, nematodes, protozoa, algae, fungi [Störmer (51)], which are then decomposed by the bacteria; or to all of these combined.

3. Microbiological balance or equilibrium. According to Hiltner and Störmer (21), the results of partial sterilization are due to a change in the bacterial flora.

4. Protozoa theory [Russell and Hutchinson (47, 48)].

5. Toxin theory [Greig-Smith (16)].

6. Destruction of fungi and bacteria which are causative agents of plant diseases [Bolley (2), Jachshevski (24)].

7. Increased nitrogen-fixation [Heinze (19), Hiltner and Störmer (21)]. Koch (27), however, maintains that nitrogen fixation by bacteria is decreased by partial sterilization.

It remains to be seen which of these theories is the correct one and whether the favorable influence of heat and antiseptics both on sick and normal soil can be explained altogether by any one or more of these theories. Even then, according to Miehe [cf. Waget (55)], soil sterilization still presents too many obscurities and uncertainties, so that it cannot be presented as a panacea for soil ills.

EXPERIMENTAL

Methods. Numbers of bacteria and actinomycetes were determined by the plate method, as described recently (57), using 5 to 10 plates for each determination. The numbers of fungi were determined by the use of a special acid medium (56), using a dilution 0.1 to 0.01 of the final dilution used for the determination of bacteria. The plates for fungi were incubated 48 to 72 hours at 25–28°C. and for bacteria, 6 to 7 days. The protozoa were determined by the dilution method using for the final dilution a 2-per cent hay infusion + 0.5 per cent NaCl and a soil infusion + 0.01 per cent powdered egg-albumen. The cultures were

examined after 5 and 14 days. Only the general groups of ciliates, amoebae and flagellates were determined, without any attempt at further differentiation.

Nitrates were determined by the phenol-disulfonic acid method and ammonia by distillation with MgO. The production of carbon dioxide in the soil was obtained by placing the proper amount of soil (usually 1 kgm.) in small earthenware pots, bringing the soil to optimum moisture (60 per cent of moisture-holding capacity), then placing the pot under a bell-jar, using an apparatus similar to the one described in detail by Neller (39). The CO₂ was absorbed in standard Ba(OH)₂ solution and titrated back with a standard solution of oxalic acid. A stream of air was passed through the pots at the rate of 3 liters per hour for 14 days, due to the fact that a short period of time may give an incorrect indication of the CO₂ production of the soil. It has been observed by van Suchtelen (54), Potter and Snyder (43) and in our own experiments that, when the soil is placed in the respiration apparatus, the CO₂ production is rapid during the first 2 to 3 days, and then diminishes. It was deemed, therefore, advisable to use a period of 14 days as a unit of time and as an index of CO₂-producing capacity of the soil. The apparatus was allowed to run all the time, without interruption.

TABLE 1
Chemical condition of soils from nitrogen plots

PLOT NO.	FERTILIZER TREATMENT	CROP YIELD PER ACRE FOR LAST 14 YEARS	NITROGEN CONTENT	CARBON CONTENT	REACTION
		lbs.	per cent	per cent	pH
5A	16 tons cow manure, minerals*	60,541	0.1463	1.73	5.5
7A	Nothing	15,295	0.0826	0.96	5.0
9A	320 lbs. NaNO ₃ , minerals	50,488	0.0994	1.17	5.8
11A	(NH ₄) ₂ SO ₄ equivalent to 320 lbs. NaNO ₃ , minerals	38,731	0.1064	1.23	4.6
7B	Lime only	27,239	0.0868	1.18	6.3

* "Minerals" are 320 lbs. potassium chloride and 640 lbs. acid phosphate per acre.

The first experiment to be reported deals with the influence of various concentrations of volatile antiseptics upon bacterial activities of soils of different fertility. In this connection the nitrogen plots of this department, which have received different fertilizer treatments for the last 15 years and where definite differences in fertility have been established have been utilized. A careful record of the crop yields of these plots has been kept and some of these plots have been submitted recently to a careful bacteriological analysis (58). Five plots were used for this purpose. Four 200-gm. portions from the soil of each plot were placed in glass jars. Three of the jars were treated with 0.1, 1.0, and 5.0 per cent of toluene, respectively. The jars were closed tightly with covers and allowed to stand 3 days. At the end of that time, the covers were taken off and the jars plugged with cotton so as to prevent the contamination of the soils with bacteria and fungi floating in the air. The toluene was, therefore, not completely evaporated for some time where the larger amounts of it were used. The moisture content of the soil was kept up by addition of sterile distilled water. Table 1 shows the treatment, crop yield, carbon and nitrogen content and reaction of the plots. The results of the toluene treatment are given in table 2.

TABLE 2
Influence of different concentrations of tolueno upon the number of microorganisms and their activities in soils differently treated

PERIOD OF INCUBA- TION	CONTROL				0.1 PER CENT OF TOLUENE				1 PER CENT OF TOLUENE				5 PER CENT OF TOLUENE							
	B+A		A	F	B+A		A	F	B+A		A	F	B+A		A	F	Protozoa			
	mil- lions	per cent of B+A	mil- lions	per cent of B+A	mil- lions	per cent of B+A	mil- lions	per cent of B+A	mil- lions	per cent of B+A	mil- lions	per cent of B+A	mil- lions	per cent of B+A	mil- lions	per cent of B+A	per cent of Protozoa			
0*	15.54	18	37	C	Fl Am	15.54	18.0	37	C	Fl Am	15.54	18	37	C	Fl Am	15.54	18	37		
	18.4	18.5	37	C	Fl Am	9.0	24.4	0.5			3.2	47	0.08			2.1	43	0.02		
	12	12.4	25.8	65	C	Fl	18.0	14.0	0	Fl	16.4	49	100			1.7	50	0.12		
	30	11.2	25	59	C	Fl	16.5	25.0	80	Fl	15.0	60	226			6.8	48	25		
	55	6.35	36	58	C	Fl	18.0	40.0	270	C	Fl	12.8	48	1,010	C	Fl	10.0	40	21	
	<i>NH₄N & NO₂-N</i>				1.74 mgm. 3.20 mgm.				2.89 mgm. 3.40 mgm.				6.93 mgm. Trace				6.58 mgm. 0.00 mgm.			
3†	0	3.0	27	31	Fl Am	3.0	27	31	Fl Am	3.0	27	31	Fl Am	3.0	27	31	Fl Am	3.0	27	31
	3	5.0	18	39	Fl Am	3.3	15	0.6		1.8	22	0.1		1.6	25	0		1.6	25	0
	12	5.5	14	39	C	Fl	16.2	5	40	Fl	1.2	0	50			0.94	0	0.12		
	30	3.7	19	33	C	Fl	12.4	9	80	Fl	2.0	0	146			0.2	0	33		
	55	3.2	28	32	C	Fl	11.8	16	166	Fl Am	10.8	17	330	Fl	2.4	0	84			
7A	<i>NH₄N & NO₂-N</i>				1.12 mgm. 0.95 mgm.				1.96 mgm. 0.12 mgm.				1.96 mgm. Trace				1.96 mgm. 0.00 mgm.			
	0	8.8	25	16	Fl Am	8.8	25	16	Fl Am	8.8	25	16	Fl Am	8.8	25	16	Fl Am	8.8	25	16
	3	10.4	20	11	Fl Am	7.3	25	1		4.0	24	0.08		2.5	25	0.02		2.5	25	0.02
	12	10.2	20	20	C	Fl	17.8	5	0	Fl	11.0	21	0			1.8	8	0.2		
9A	30	8.3	19	39	C	Fl	18.0	11	85	Fl	11.5	50	180			2.6	15	24		
	55	6.6	26	18	C	Fl	24.5	20	280	C	Fl	10.4	46	300	C	Fl	8.1	16	54	
	<i>NH₄N & NO₂-N</i>				1.62 mgm. 2.20 mgm.				2.10 mgm. 2.20 mgm.				3.92 mgm. Trace				3.64 mgm. 0.00 mgm.			

11A	0	5.1	9	112	C Fl	5.1	9	112	C Fl	5.1	9	1112	C Fl
	3	6.8	7	88	C Fl	3.5	9	8.2	Fl	1.4	19	0.04	Tr.
	12	6.1	7	97	C Fl	6.8	4	0	Fl	1.6	0	0	0
	30	2.2	8	118	C Fl	7.5	8	80	Fl	1.8	5	200	Fl
	55	2.6	14	101	C Fl	2.4	15	340	Fl	2.04	10	540	Fl
	<i>NH₃-N</i> <i>NO₂-N</i>		1.33 mgm. 1.90 mgm.		3.08 mgm. 0.14 mgm.		3.08 mgm. Trace		3.92 mgm. 0.00 mgm.				
7B	0	6.5	37	9	C Am	6.5	37	9	C Am	6.5	37	9	C Am
	3	8.1	25	13	C Fl Am	35.0	6	1.4	C Fl	3.4	31	0.02	Am
	12	8.6	22	7	C Fl	35.9	5	40	C Fl	16.2	10	2	0.02
	30	7.3	27	22	C Fl	38.0	9	44	Fl Am	22.0	11	24	13.6
	55	7.03	32	23	C Fl	25.8	14	50	C Fl	22.8	21	86	Fl Am
	<i>NH₃-N</i> <i>NO₂-N</i>		1.12 mgm. 1.60 mgm.		1.33 mgm. 1.65 mgm.		2.24 mgm. 0.56 mgm.		2.87 mgm. 0.00 mgm.				

* Counts made just before treatment with toluene.

† Counts made on opening flasks. After this sterile water was added to bring soils to optimum moisture.

‡ B = bacteria; A = actinomycetes; F = ciliates; C = fungi; Fl = flagellates; Am = amoebae.

§ NH₃-N and NO₂-N are given as milligrams per 100 gm. of soil after 55 days' incubation.

In the case of the untreated soils, a stimulating effect upon numbers of microorganisms was always obtained as a result of mixing, sieving and bringing up to optimum moisture. This increase was followed, after a few days, by a steady decrease. It is important to note that the percentage of actinomycetes varied usually inversely with the total number of microorganisms developing on the plate, exclusive of fungi, *i.e.*, the percentage of actinomycetes decreased when the total number increased and the actinomycetes ratio began to increase, when the total number began to decrease pointing to the fact that the latter group of organisms is not subject to as rapid changes as the true bacteria developing on the plate. Increases or decreases in the number of actinomycetes take place much more slowly than in the case of bacteria. The numbers of fungi usually tend to increase as a result of incubation in the laboratory, except soil 11A which is already very rich in fungi. All the three major groups of protozoa (ciliates, flagellates, amoebae) were present in the control soils, although the amoebae were not always demonstrated.

In some cases 0.1-per-cent toluene caused a decrease in the number of bacteria followed by an increase or, as in the case of 7A and 7B, it brought about directly a decided increase in the number of bacteria. The protozoa were at first destroyed (except 7B), but later developed again, first the flagellates, then the amoebae and ciliates. It is interesting to note that the greatest stimulus upon the number of bacteria and actinomycetes developing on the plate was brought about in 7B, where the protozoa remained alive and active even after three days treatment with 0.1-per-cent toluene. Although the small amount of toluene was not sufficient to kill the protozoa in this soil, the stimulus exerted upon bacterial development is most pronounced. The fungi were practically destroyed by the 0.1-per-cent toluene and the percentage of actinomycetes was appreciably reduced. The fungi, however, soon began to multiply very rapidly and after 30-50 days greatly exceeded the numbers originally present. After 55 days, as a result of treatment with 0.1-per-cent toluene, sample 5A contained only about 20 per cent more bacteria, more than twice as many actinomycetes and over seven times as many fungi, while the protozoa were as active as at the start; sample 7A contained four times as many bacteria, a smaller percentage of actinomycetes and over five times as many fungi, with the same abundance of protozoa; sample 9A contained three times as many bacteria, a smaller percentage of actinomycetes and seventeen times as many fungi; sample 11A contained a smaller number of bacteria, a higher percentage of actinomycetes and a greater number of fungi; and sample 7B contained four times as many bacteria, much lower percentage of actinomycetes and five and a half times as many fungi.

A small amount of toluene is thus found to have a destructive effect upon the fungi but a decidedly stimulating effect upon bacteria and temporary depressing effect upon protozoa. By it the soil is made a much better medium for the development of fungi.

As stated above, the soils were not spread out for the evaporation of the toluene in order to prevent reinoculation with dust fungi; the tight covers were merely replaced by cotton plugs. However, this did not prevent the contamination of the soil and it did prevent the rapid evaporation of toluene in the case of 1.0-per-cent concentration and especially where 5 per cent has been added.

One per cent of toluene produced a much greater depressive effect upon the bacteria and, due to the slow evaporation of the toluene, it took a somewhat longer period of time for bacterial development to take place. The depression was followed in all cases by a rise in numbers reaching in three out of five soils after 55 days a point much above the original number. Here again the soil was made a much better medium for the development of fungi, which reached even higher numbers than in the case of the treatment with 0.1 per cent of toluene. It is interesting to note that in the two soils (5A and 11A), where the numbers of bacteria were after 55 days lower than at start, the numbers of fungi were the highest of all soils at all periods, reaching over one million and one-half million, respectively. While there were at the beginning of the experiment three times as many fungi in 11A as in 5A, 5A contained twice as many fungi as 11A 55 days after treatment with 1 per cent of toluene. Fungi are directly stimulated by the addition of available organic matter. Since 5A has a much greater content of organic matter than 11A, the above results indicate that the toluene treatment brought about a greater availability of the organic matter in the soil (plate 1).

The protozoa were destroyed by 1 per cent of toluene in all soils, but after 55 days they were found again. It is of importance to point out the great abundance of all the three groups of protozoa in 7B, which contains also the highest number of bacteria, but the lowest number of fungi.

In the case of the soils treated with 5 per cent of toluene, the disinfectant was still present after 15-20 days. This lasting effect of the disinfectant resulted in a much greater reduction of the bacteria followed only by a late increase, while the protozoa disappeared completely. Outside of this, one can hardly draw any further conclusions from this treatment, except as to the ammonia content.

The numbers of bacteria, actinomycetes, fungi and protozoa in the soil did not show, as a result of toluene treatment, any correlation with soil fertility, or organic matter content of a soil; as a matter of fact the most fertile soil (5A) showed the least increase in the number of bacteria (and actinomycetes), while the least fertile, but limed, soil showed the greatest increase. This may perhaps be correlated with the inverse development of fungi since 5A showed the greatest development of fungi as a result of toluene treatment and 7B the least. *The formation of ammonia, however, is directly dependent on the organic-matter content of the soil and is not correlated with the increase in the numbers of bacteria, when the differently treated soils are compared.* Soil 5A gave the greatest increase in the amount of ammonia, as a result of toluene

treatment; however the gain over the control is more apparent than real. For 1 and 5 per cent of toluene killed or temporarily put out of action the nitrifying bacteria and the ammonia formed was not nitrified. When we compare the total soluble nitrogen produced, we find 4.94 mgm. for the control, 6.20 mgm. for 0.1 per cent of toluene, 6.93 mgm. for 1 per cent and 6.58 mgm. for the 5 per cent of toluene treatment. The greatest gain is found between the control and 0.1 per cent of toluene treatment; protozoa were found in the latter soil 12 days after treatment, so that surely they had enough time within the 55 days to stop bacterial development. Exactly the same is true, only to a lesser extent of soil 9A. Soils 11A and 7B did not show any appreciable gain of soluble nitrogen in the toluene treated soils over the controls. Soil 7A contained the lowest amount of organic matter and it is only natural to find the lowest amount of ammonia formed, but here again, the toluene treatment did not result in any greater increase in soluble inorganic nitrogen than the control.

The results of the above experiment lead us to conclude that the treatment of an ordinary field soil with toluene will bring about a change in the different ratios between the various groups of soil microorganisms as present in the soil: the total number of bacteria and actinomycetes first decreases as a result of treatment followed by an increase; the larger the amount of toluene applied, the greater will be the decrease in bacterial numbers and the more delayed will be the increase following. The ratio of actinomycetes to the total number of microorganisms developing on the plate decreases with an increase in the latter, but is finally followed by an increase.

Treatment of soil with toluene had a marked influence upon the development of the fungi. These organisms were nearly all destroyed as a result of toluene treatment, but some of them seem to have survived and have developed so rapidly that the numbers soon greatly exceeded those in the original soil. The surviving fungi belonged only to very few species, as could be readily recognized from the plates, perhaps not more than three or four, especially the common soil *Zygorhynchus* and a certain pink *Penicillium*.

Soil treated with toluene is made a better medium for the growth of a few specific fungi. Although the protozoa were at first destroyed, especially the flagellates, they reappeared after some time, depending on the amount of disinfectant applied; in view of the fact that in certain soils (7B) the greatest increase in bacterial development coincides with little injury to protozoa, one might be justified in concluding from these experiments that an increase in the numbers of bacteria and in the decomposition of organic matter in the particular soil is not necessarily correlated with the absence or presence of protozoa.

The above experiment was repeated, with soils from only plots 5A, 7A and 7B. The soil was placed in 2-kgm. portions in large pots and brought to optimum moisture content. One pot of each soil was left as control, two pots were treated with 2 per cent of toluene for 48 hours and two were

heated (by placing in hot water, with thermometer in center of soil) for 1 hour at 65–75°C. After 48 hours the toluened soil was spread out for 4 hours to allow the toluene to evaporate. The soil was then returned to the pots and brought back to weight with sterile distilled water. One of the two treated pots was left without further treatment and to the other one 5 per cent of fresh soil was added and well mixed in. The pots were then kept covered in the incubator at 25–28°C. At frequent intervals, samples were taken for the determination of numbers of bacteria and actinomycetes, fungi, ammonia- and nitrate-nitrogen. The pots were kept at the same moisture content. Results are given in table 3.

Here again we find that the control soils (5A and 7B), when brought under optimum moisture and temperature conditions, show at first a slight increase in the number of microorganisms, followed by a constant decrease. Soil 7A shows more or less uniform numbers for the first month. The discrepancy in the behavior of 7A in this experiment from the previous one may be due to the fact that this time the soil was sampled in April when the moisture was at an optimum, while the previous experiment was carried on in the fall. The ammonia in the control soil is present always only in small amounts while, on continued incubation, it even tends to diminish because of its transformation into nitrates. The latter continuously accumulate in the incubated untreated soil. The total soluble nitrogen constantly increases in the manured soil (5A) which is rich in organic matter, while it remains on a level in the two unmanured plots. At the beginning all the three plots contained about 2 mgm. of soluble nitrogen in 100 gm. of soil; at the end of 31 days' incubation, 5A contained about twice as much soluble nitrogen, or 3.68 mgm., while 7A and 7B contained only 1.84 and 2.06 mgm. respectively, or just about the same as when freshly sampled.

Toluene treatment exerted a characteristic influence upon the numbers of microorganisms in the soil and upon ammonia accumulation, similar to that observed by other investigators and in our first experiment. The total numbers were depressed as a result of the treatment, but soon began to increase greatly exceeding the untreated soil. The same is true, but to a much more striking extent of the fungi. Toluene almost completely depressed this group of organisms in the soil but they soon began to multiply again, especially so in the reinoculated soil. The three soils behave differently after toluene treatment. The slightly acid soil 5A, rich in organic matter, allowed only a fair increase in the number of bacteria (including the actinomycetes) so that in 30 days this soil contained over twice as many bacteria as the untreated control soil. The numbers of fungi which were diminished from 34,000 to 65 per gram or practically completely repressed as a result of toluene treatment, have increased in the uninoculated soil to 132,000 and in reinoculated soil to 190,000 per gram; *i.e.*, to four and nearly six times the number of those of the control soil. In 7B, the neutral, limed soil, rather poor in organic matter, the numbers of bacteria, originally less than in 5A, were repressed to a

TABLE 3
Influence of volume and heat upon the number of microorganisms in the soil and their activities

PLOT NUMBER	LENGTH OF INCUBATION PERIOD	CONTROL						TOLUENE (2 FLR CENT FOR 48 HOURS)						
		N in 100 gm. soil			Uninoculated			Reinoculated with 5 per cent of fresh soil			N in 100 gm. soil			
		B + A*	A*	F	NH ₄ -N	NO ₃ -N	B + A	A	F	NH ₄ -N	NO ₃ -N	B + A	A	F
5A	0†	14,100	16	34	1.44	0.30	5,100	40	0.065	2.24	0.21	5,500	41	0.13
	7	15,000	25	38	1.44	0.80	9,760	15	1	4.03	0.08	9,000	19	3
	15	12,000	27	35	0.86	1.40	13,000	20	35	4.90	0.06	16,000	22	65
	31	9,500	23	34	0.58	3.10	21,800	36	132	6.01	0.04	28,500	25	190
	43	7,800	32	31	0.86	4.10	31,000	40	470	6.05	0.02	33,000	25	560
	60	8,600	31	29	0.43	4.60	39,500	41	363	6.10	0	41,000	36	370
	105	5,100	36	30	0.14	6.80	15,200	35	490	7.20	2.7	11,600	41	390
	0	6,800	25	43	1.68	0.20	2,100	23	0.2	2.00	0.17	1,860	32	0.13
	7	6,700	23	35	1.68	0.28	4,600	13	2	1.44	0.13	12,200	8	26
	15	6,600	24	38	0.86	0.45	15,000	15	44	1.73	0.13	22,000	5	52
7A	31	6,900	23	36	1.14	0.70	12,000	25	68	2.59	0.11	15,000	4	101
	43	4,800	25	48	0.86	1.20	9,400	20	110	1.87	0.08	13,400	5	304
	60	4,900	26	42	0.14	1.42	15,600	25	133	1.44	0.11	16,800	6	260
	105	4,700	16	0	1.60	7,700	15	200	3.74	0.18				1.87
	0	10,900	24	12	1.68	0.05	3,800	53		1.68	0.03	5,000	47	0.13
7B	7	14,100	26	10	1.14	0.25	4,200	22		2.30	0.03	63,400	6	7
	15	10,200	25	12.5	1.12	0.60	35,000	6		2.59	0	70,000	4	16
	31	7,800	27	16	0.86	1.20	30,000	8	2.6	2.30	0	44,500	5	28
	43	8,400	33	11	0.86	1.30	36,000	6	3	3.17	0	54,000	5	20
	60	7,900	36	10.6	0.29	1.60	48,000	16	3	2.45	0	48,500	14	8.3
105	7,600	34	8	0.10	2.60	30,600	11	2.6	0.30	3.20	33,400	11	8	0.3
													3.20	3.20

PLOT NUMBER	LENGTH OF INCUBA- TION PERIOD <i>days</i>	HEATED (65-75° C. FOR 1 HOUR)						Renoculated with 5 per cent of fresh soil						
		Uninoculated			N in 100 gm. soil			B + A			F		N in 100 gm. soil	
		B + A	A	F	NH ₄ -N	NH ₄ -N	mgm.	thousands	per cent	A	F	NH ₄ -N	mgm.	
SA	0†	1,600	12	8	2.00	0.26	1,100	4	0.13	1.68	0.29			
	7	10,600	17	43	3.74	0.25	42,600	22.5	83	3.17	0.35			
	15	12,000	15	68	4.61	0.30	45,000	24	160	3.74	0.76			
	31	11,000	17	56	5.18	0.20	58,000	22	170	3.17	2.40			
	43	24,000	10	57	5.04	0.21	51,000	39	172	1.58	4.80			
	60	33,000	9	146	5.18	0.04	43,500	42	167	0.72	5.30			
TB	105	18,500	12	180	5.90	0.90	23,600	42	140	0.50	6.50			
	0	1,700	13	0.065	1.68	0.06	900	3		1.68	0.06			
	7	27,000	8	0.6	2.30	0.08	46,400	4	7.3	3.17	0.12			
	15	42,000	5	1	2.30	0.13	48,000	2	38	3.17	0.17			
	31	33,000	10	0.7	1.73	1.50	28,500	6	32	2.06	1.70			
	43	26,000	10	3	1.44	1.70	33,500	7	46	0.72	2.10			
	60	35,500	6	0.7	0.87	1.40	24,000	4	8.3	0.29	1.60			
	105	26,000		0.7	0.20	3.20	23,400	4	9.3	0.10	3.20			

* B + A = bacteria and actinomycetes; A = actinomycetes, per cent of colonies developing on plate; F = fungi; NH₄-N = ammonia nitrogen; NO₃-N = nitrate nitrogen.

† Incubation was started soon after toluene was evaporated or heating of soil was completed.

greater extent by the toluene; this was followed by an increase so that in 15 days there were 35,000,000 and 70,000,000 in the uninoculated and reinoculated soils respectively; *i.e.*, three and a half and seven times as much as those of the control. The fungi, however, in this very soil, multiplied only very slowly even when reintroduced. The microbial flora in 7A behaved in a similar way as in 5A, never reaching such large numbers as in the latter undoubtedly because of the lower content of organic matter.

It is interesting to note here that 5A was found to contain after 15 days' incubation both amoebae and flagellates in the uninoculated and reinoculated soils, while 7B contained flagellates in the reinoculated soil and no protozoa in the uninoculated soil. Soil 7A was free from protozoa. In 43 days, there was an abundance of protozoa, chiefly small amoebae and flagellates in all the soils. As a matter of fact, the toluene-treated and reinoculated soils contained larger numbers of amoebae than the control soils. The uninoculated soils contained fewer protozoa. There was no correlation, however, between the numbers of bacteria and development of protozoa.

There was a slight increase in ammonia as a result of toluene treatment, especially in soil 5A. The ammonia continuously increased in soil 5A, both in the uninoculated and reinoculated soils, while the nitrifying bacteria became active in both cases only after 60 days. The increase in ammonia was only slight in soil 7A, while it actually decreased in the reinoculated soil. There was a definite increase in ammonia content in soil 7B, a part of which was converted into nitrates in the reinoculated soil, in which the nitrifying bacteria became more active than in the unlimed soils, once reintroduced.

When we compare the curves for bacteria, fungi and ammonia (fig. 1, 2, 3) for soils 5A, 7A, and 7B, we find that the ammonia accumulation does not go hand in hand with the increase in bacteria: but that there is much less ammonia formed in soil 7B with a much greater bacterial flora than in soil 5A. We could explain the ammonia accumulation by the fungus curve, but even this would not be the whole explanation.

Soil 5A is rich in organic matter and acid in reaction, therefore it favors fungus development; soil 7A is even more acid in reaction but poor in organic matter, and we would, therefore, expect that any fungus development taking place in this soil would be at the expense of the soil nutrients; soil 7B is nearly neutral in reaction and is poor in organic matter, we would then expect a limited fungus development, independent, of course, of the development of protozoa and bacteria. The latter, however, are markedly influenced by the development of fungi. A high fungus flora in a soil rich in organic matter (5A) seems to have some relation to the rather limited increase in bacteria, in comparison with a soil (7B) not favoring the development of fungi. The accumulation of ammonia depends upon the abundance of organic matter in the soil, the amount of ammonia used up by the soil organisms and that transformed into nitrates. Soil 5A, rich in organic matter allows a large development of bacteria and fungi and a high accumulation of soluble nitrogen.

Soil 7A, acid in reaction and low in organic matter, allows a limited development of bacteria, a high development of fungi and, as a result of these two phenomena, a low accumulation of soluble nitrogen. Soil 7B, neutral in reaction but low in organic matter, allows a high development of bacteria, low development of fungi, and, as a result of these two phenomena, a comparatively high accumulation of soluble nitrogen.

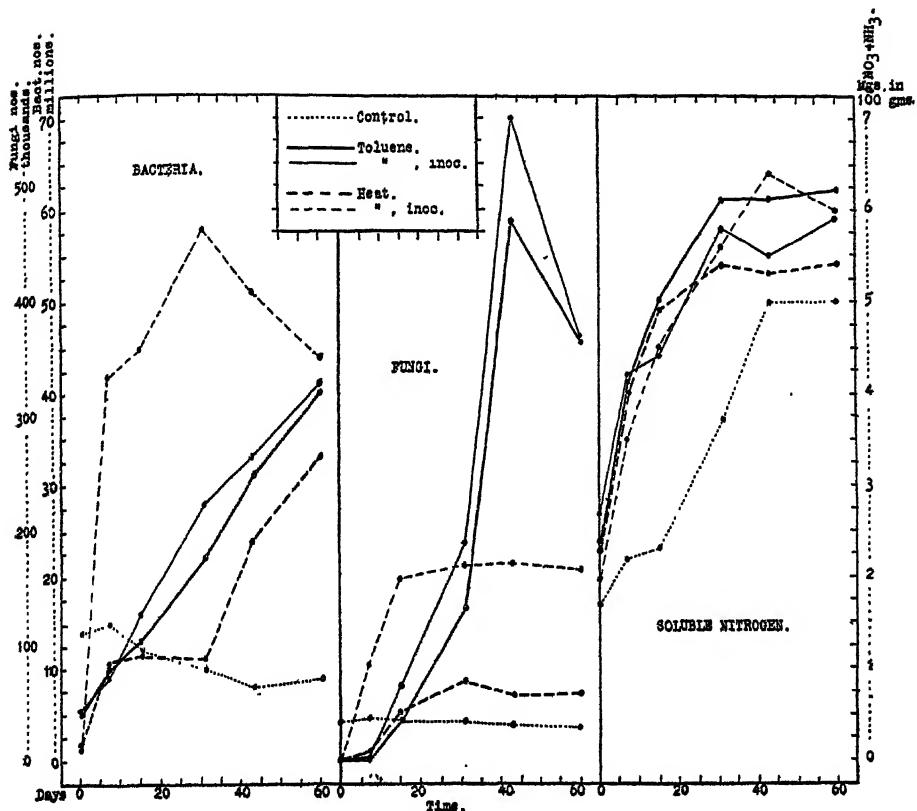


FIG. 1. INFLUENCE OF TOLUENE AND HEAT UPON NUMBERS OF BACTERIA, FUNGI AND ACCUMULATION OF SOLUBLE NITROGEN IN AN ACID SOIL RICH IN ORGANIC MATTER (5A)

Heating the soil produced about the same effect as treatment with toluene. Bacteria increased at first in 5A only to a limited extent in the uninoculated soil, but very markedly when the soil was reinoculated. Fungi increased in both cases rapidly, more so in the reinoculated soil. Bacteria increased rapidly in soil 7B in both uninoculated and reinoculated soils, while the fungi multiplied rapidly only when reinoculated. A great deal of ammonia was formed in soil 5A, a part of which was transformed into nitrates in the reinoculated

soil. Some ammonia was formed also in soil 7B, less in the uninoculated than the reinoculated soil, possibly due to the more abundant development of fungi in the latter. The nitrifying bacteria became active in the heated soil more rapidly than in the toluene-treated soil, especially when reinoculated. A detailed discussion of the metabolism of bacteria, fungi and actinomycetes as bearing upon these results will be published later.

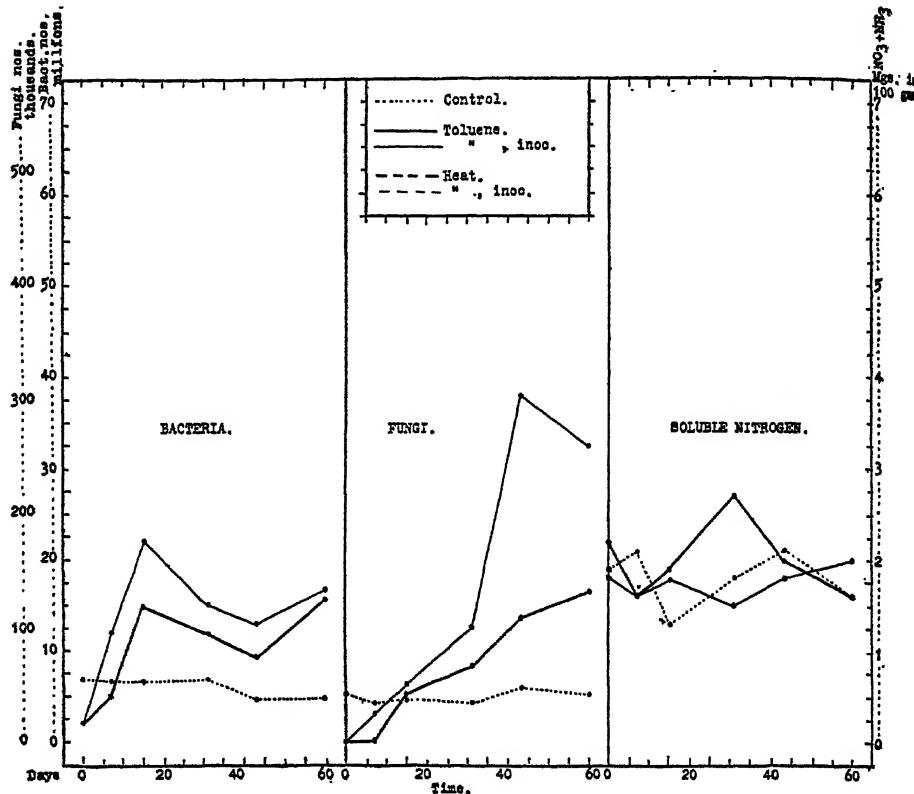


FIG. 2. INFLUENCE OF TOLUENE UPON NUMBERS OF BACTERIA, FUNGI AND ACCUMULATION OF SOLUBLE NITROGEN IN AN UNLIMED ACID SOIL POOR IN ORGANIC MATTER (7A)

SUMMARY

1. The results of a study on the influence of toluene and heat upon the microbiological population of variously treated soils are reported.
2. Toluene and heat influence markedly not only the development of bacteria and protozoa in the soil but also that of the actinomycetes and especially the fungi.
3. The results on the influence of toluene and heat upon bacteria and protozoa agree with those of previous investigators.

4. The fungi are repressed very markedly by toluene and heat, but soon begin to develop, especially when reintroduced, and reach numbers greatly in excess of the untreated soil. The fungi developing in the partially sterilized soils are limited to only a few species.

5. Ammonia accumulates in the partially sterilized soils in excess over the untreated soil, especially in soils rich in organic matter, but in poorer soils the rapid development of fungi may lead to a partial utilization of the ammonia.

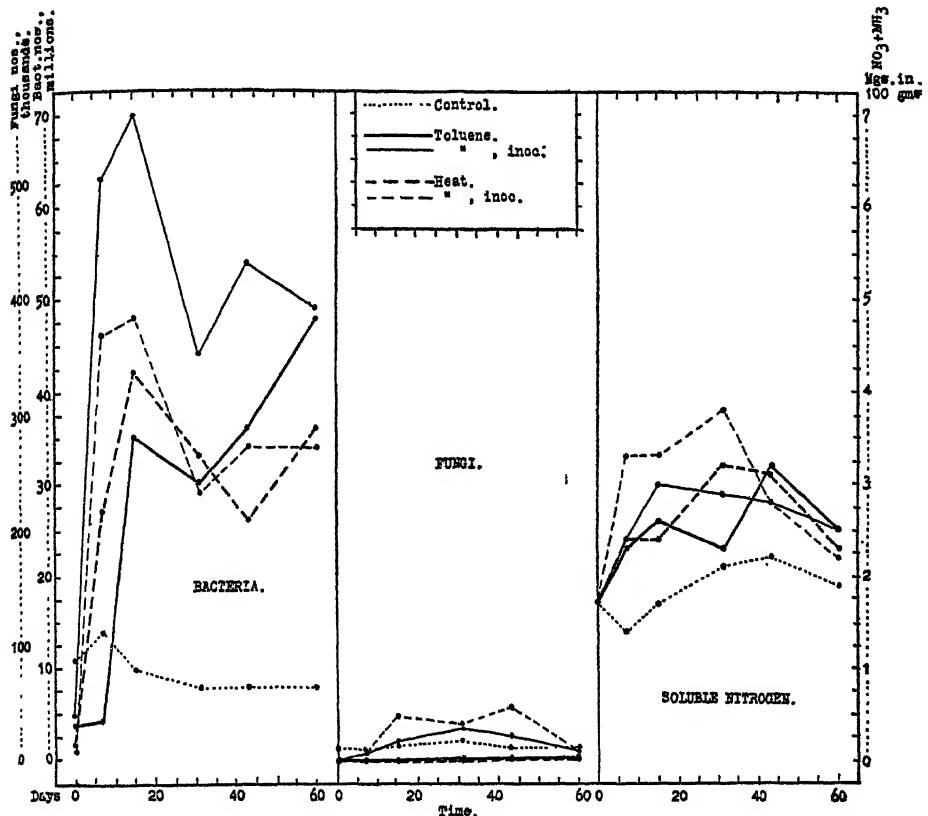


FIG. 3. INFLUENCE OF TOLUENE AND HEAT UPON NUMBERS OF BACTERIA, FUNGI AND ACCUMULATION OF SOLUBLE NITROGEN IN A LIMED, BUT SLIGHTLY ACID SOIL POOR IN ORGANIC MATTER (7B)

6. There is no correlation between the increase in bacterial numbers and accumulation of ammonia, when we compare soils containing different amounts of organic matter.

7. It is possible that the protozoa become a limiting factor to bacterial development in certain abnormal soils, such as sewage-treated soils or cer-

tain greenhouse soils, where the soil is practically saturated with moisture and in the presence of a great abundance of organic matter. However, in the case of normal soils, we should consider the part played by fungi and actinomycetes, in addition to bacteria, in the decomposition of organic matter, the influence of the abundant development of those organisms upon bacterial numbers, the influence of kind and amount of organic matter upon the formation of ammonia and multiplication of bacteria, before we can attempt to explain the limitation of the bacteria.

REFERENCES

- (1) ALIEKSIEIEV, A. G. 1917 Protistic coprology, as a special branch of protistology, and description of several new species of protists "coprococae" (Russian). *In Jour. Microb.*, v. 4, p. 97-134.
- (2) BOLLEY, H. L. 1910-1913 Interpretation of results in experiments upon cereal cropping methods after soil sterilization. *In Science*, v. 32, p. 529-541; v. 33, p. 229-234; v. 38, p. 48-50, p. 249-259; also N. D. Agr. Exp. Sta. Bul. 107.
- (3) BOYOUOS, G. J., AND McCOOL, M. M. 1915 The freezing point method as a new means of measuring concentration of the soil solution directly in the soil. *In Mich. Agr. Exp. Sta. Tech. Bul.* 24.
- (4) BUDDIN, W. 1914 Partial sterilization of soil by volatile and non-volatile antiseptics. *In Jour. Agr. Sci.*, v. 6, p. 417-451.
- (5) CRABTREE, J. 1914 The functions of the non-bacterial population of the "bacteria-bed." *In Centbl. Bakt. (etc.)*, Abt. 2, v. 40, p. 225-239.
- (6) CUTLER, D. W. 1923 The action of protozoa on bacteria when inoculated into sterile soil. *In Ann. Appl. Biol.*, v. 10, p. 137-141.
- (7) CUTLER, D. W., CRUMP, L. M., AND SANDON, H. 1922 A quantitative investigation of the bacterial and protozoan population of the soil, with an account of the protozoan fauna. *In Phil. Trans. Roy. Soc. (London)*, Ser. B., v. 211, p. 317-350.
- (8) DARBIshire, F. V., AND RUSSELL, E. J. 1908 Oxidation of soils and its relation to productiveness. II. The influence of partial sterilization. *In Jour. Agr. Sci.*, v. 2, p. 305-326.
- (9) FISCHER, H. 1909 Versuche über Bakterienwachstum in sterilisiertem Boden. *In Centbl. Bakt. (etc.)*, Abt. 2, v. 22, p. 671-675.
- (10) FRANCÉ, R. H. 1921 Das Edaphon, 2d ed. Stuttgart. Franckh.
- (11) FRED, E. B. 1911 Über die Beschleunigung der Lebenstätigkeit höherer und niederer Pflanzen durch kleine Giftmengen. *In Centbl. Bakt. (etc.)*, Abt. 2, v. 31, p. 185-245.
- (12) FRED, E. B. 1916 Relation of carbon bisulphid to soil organisms and plant growth. *In Jour. Agr. Res.*, v. 6, p. 1-19.
- (13) GAINEY, P. L. 1912 The effect of toluol and CS₂ upon the micro-flora and fauna in the soil. *In Mo. Bot. Gard.*, v. 21, p. 147-169; also *in Soil Sci.*, v. 3, p. 353.
- (14) GAINEY, P. L. 1914 Effect of CS₂ and toluol upon nitrification. *In Centbl. Bakt. (etc.)*, Abt. 2, v. 39, p. 584-595.
- (15) GOODEY, T. 1915 Investigations on protozoa in relation to the factor limiting bacterial activity in soil. *In Proc. Roy. Soc. (London)*, ser. B., v. 88, p. 437-456.
- (16) GREIG-SMITH, R. 1911 The bacteriotoxin and the agricere of soils. *In Centbl. Bakt. (etc.)*, Abt. 2, v. 30, p. 552.
- (17) GREIG-SMITH, R. 1912 The inactivity of soil protozoa. *In Proc. Lin. Soc. N. S. Wales*, v. 37, p. 655-672.
- (18) GREIG-SMITH, R. 1917 The action of certain microorganisms upon the numbers of bacteria in the soil. *In Proc. Lin. Soc. N. S. Wales*, v. 42, p. 162-166.
- (19) HEINZE, B. 1906 Einiges über das Schwefelkohlenstoff, dessen Wirkung auf niedere pflanzliche Organismen, sowie seine Bedeutung für die Fruchtbarkeit des Bodens. *In Centbl. Bakt. (etc.)*, Abt. 2, v. 16, p. 329-358.

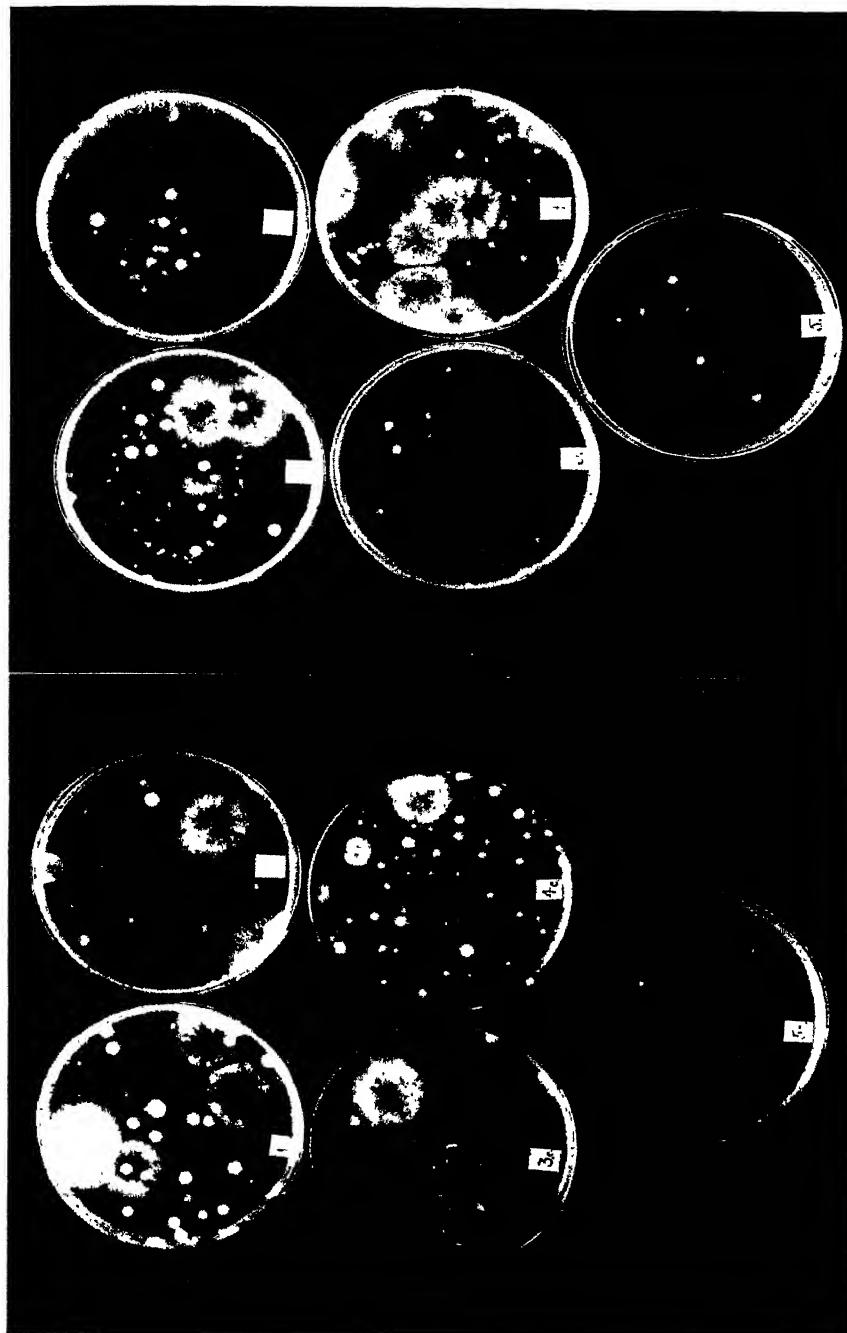
- (20) HEINZE, B. 1907 Einige weitere Mitteilungen über den Schwefelkohlenstoff und die CS₂ Behandlung des Bodens. *In* Centbl. Bakt. (etc.), Abt. 2, v. 18, p. 56-74, 246-264, 462-470, 624-634, 790-798.
- (21) HILTNER, L., AND STÖRMER, K. 1903 Studie über die Bakterienflora des Ackerbodens, mit besonderer Berücksichtigung ihres Verhaltens nach einer Behandlung mit Schwefelkohlenstoff und nach Brache. *In* Arb. K. Gsndhtsam., Biol. Abt., v. 3, p. 445-545.
- (22) HUTCHINSON, H. B. 1913 The partial sterilization of the soil by means of caustic lime. *In* Jour. Agr. Sci., v. 5, p. 320-330.
- (23) HUTCHINSON, H. B., AND MACLENNAN, K. 1914 The relative effect of lime as oxide and carbonate on certain soils. *In* Jour. Agr. Sci., v. 6, p. 302-322.
- (24) JACHSHEVSKI, A. 1912 On the causes which determine infertility of the soil and loss of crops. *In* Khosiaistvo (Kiev), v. 7, no. 34, p. 1103-1108; *Ref. in* Internat. Inst. Agr. Bul. Agr. Intel. Pl. Dis., v. 3, p. 2528-2531.
- (25) KELLEY, W. P. 1915 Ammonification and nitrification in Hawaiian soils. Hawaii Agr. Exp. Sta. Bul. 37.
- (26) KOCH, A. 1899 Untersuchungen über die Ursachen der Rebenmüdigkeit mit besonderer Berücksichtigung der Schwefelkohlenstoffbehandlung. Arb. Deut. Landw. Gesell., v. 40, p. 44; *also in* Centbl. Bakt. (etc.), Abt. 2, v. 5, p. 660.
- (27) KOCH, A., LITZENDORFF, J., KRULL, F., AND ALVES, A. 1907 Die Stickstoffanreichung des Bodens durch freilebende Bakterien und ihre Bedeutung für die Pflanzenernährung. *In* Jour. Landw., v. 55, p. 355-416.
- (28) KÖNIG, J., HASENBÄUMER, J., AND GLENK, K. 1913 Über die Anwendung der Dialyse und die Bestimmung der Oxydationskraft für die Beurteilung des Bodens. *In* Landw. Vers. Stat., v. 79-90, p. 491-534.
- (29) KOPELOFF, N., COLEMAN, D., AND LINT, H. C. 1917 A review of investigations in soil protozoa and soil sterilization. *In* Soil Sci., v. 3, p. 197-269.
- (30) KRÜGER, W., AND SCHNEIDEWIND, W. 1899 Ursache und Bedeutung der Salpeterzersetzung im Boden. *In* Landw. Jahrb., v. 28, p. 217-252.
- (31) KRUSE, W. 1910 Allgemeine Mikrobiologie. Vogel. Leipzig.
- (32) LÖHNIS, F. 1910 Handbuch der landwirtschaftlichen Bakteriologie, p. 714. Borntraeger. Berlin.
- (33) MANN, H. H., JOSHI, N. V., AND KANITKAR, N. V. 1912 The "rab" system of rice cultivation in Western India. *In* Mem. Dept. Agr. India, Chem. Ser., v. 2 no. 2, p. 141-192.
- (34) MILLER, F. 1914 Über den Einfluss des Kalkes auf die Bodenbakterien. *In* Ztschr. Gärungsphysiol., v. 4, p. 194-206.
- (35) MOORE, G. T. 1912 Microorganisms of the soil. *In* Science, N. S., v. 36, p. 609-616.
- (36) MORITZ, J., AND SCHERPE, R. 1904 Über die Bodenbehandlung mit Schwefelkohlenstoff und ihre Einwirkung auf das Pflanzenwachstum. *In* Arb. K. Gsndhtsam., Biol. Abt., v. 4, pt. 2, p. 123-156.
- (37) NADSON, G. A., AND ZOLKIEWICZ, A. I. 1922 *Spicaria purpurogenes* n.sp. On the antagonism of microorganisms (Russian). Bul. Jard. Bot. Repub. Russe., v. 21, Add. 1, p. 1-18.
- (38) NASIR, S. M. 1923 Some preliminary investigations on the relationship of protozoa to soil fertility with special reference to nitrogen fixation. *In* Ann. Appl. Biol., v. 10, p. 122-133.
- (39) NELLER, J. R. 1918 Studies on the correlation between the production of carbon dioxide and the accumulation of ammonia by soil organisms. *In* Soil Sci., v. 5, p. 225-241.
- (40) OLDENBACH, C. 1922 Stimulation of plants by CS₂. *In* Bul. Torrey. Bot. Club, v. 49, p. 375-390.
- (41) PETERS, R. A. 1921 The substance needed for the growth of a pure culture of *Colpidium colpoda*. *In* Jour. Physiol., v. 55, p. 7-32.
- (42) PICKERING, S. U. 1910 The activities of heat and antiseptics on soils. *In* Jour. Agr. Sci., v. 3, p. 32-54, 258-276, 277.

- (43) POTTER, R. S., AND SNYDER, R. S. 1916 Carbon dioxide production in soils and carbon and nitrogen changes in soils variously treated. *Iowa Agr. Exp. Sta. Res. Bul.* 39.
- (44) RAHN, O. 1908 Bakteriologische Untersuchung über das Trocknen des Bodens. *In Centrbl. Bakt. (etc.), Abt. 2, v. 20,* p. 38-61.
- (45) RITTER, G. 1912-1913 Das Trocknen der Erden. *In Centbl. Bakt. (etc.), Abt. 2, v. 31,* p. 116-143; *v. 36,* p. 346.
- (46) RUSSELL, E. J. 1913 The complexity of the microscopic population of the soil. *In Science, n. s., v. 37,* p. 519-522.
- (47) RUSSELL, E. J., AND HUTCHINSON, H. B. 1909 The effect of partial sterilization of soil on the production of plant food. *In Jour. Agr. Sci., v. 3,* p. 111-144.
- (48) RUSSELL, E. J., AND HUTCHINSON, H. B. 1913 The effect of partial sterilization on the production of plant food. II. The limitation of bacterial numbers in normal soils and its consequences. *In Jour. Agr. Sci., v. 5,* p. 152-221.
- (49) SCHERPE, R. 1909 Über den Einfluss des Schwefelkohlenstoffs auf die Stickstoffumsetzungsorgänge im Boden. *In Arb. K. Gsndhtsamts., Biol. Abt., v. 7, pt. 3,* p. 353-428.
- (50) STOKLASA, J. 1911 Biochemischer Kreislauf des Phosphat-Ions im Boden. *In Centbl. Bakt. (etc.), 2, Abt. v. 29,* p. 185.
- (51) STÖRMER, K. 1907 Über die Wirkung des Schwefelkohlenstoffs und ähnlicher Stoffe auf den Boden. *In Jahresber. Angew. Bot., v. 5,* p. 113-131.
- (52) STÖRMER, K. 1908 Über die Wirkung des Schwefelkohlenstoffs und ähnlicher Stoffe auf den Boden. *In Centbl. Bakt. (etc.), Abt. 2, v. 20,* p. 282-286.
- (53) TRUFFAUT, G., AND BEZSONOFF, N. 1920-1922 Influence de la sterilization sur la flore microbienne du sol. *In Compt. Rend. Acad. Sci. (Paris), v. 170,* p. 1270-1279; *v. 171,* p. 268-271; *v. 175,* p. 868-870.
- (54) VAN SUCHTELEN, F. H. H. 1910 Über die Messung der Lebenstätigkeit der aerobiotischen Bakterien im Boden durch die Kohlensäureproduktion. *In Centbl. Bakt. (etc.), Abt. 2, v. 14,* p. 45-89.
- (55) WAGET, P. 1920-1921 Sterilization et disinfection du sol. *In Rev. Prod. Chim. no. 22, 1920,* p. 655; no. 4, p. 115; no. 6, p. 183, 1921.
- (56) WAKSMAN, S. A. 1922 A method for counting the numbers of fungi in the soil. *In Jour. Bact., v. 7,* p. 339-341.
- (57) WAKSMAN, S. A. 1922 Microbiological analysis of soil as an index of soil fertility. II. Methods of the study of numbers of microorganisms in the soil. *In Soil Sci., v. 14,* p. 283-298.
- (58) WAKSMAN, S. A. 1922 Microbiological analysis of soil as an index of soil fertility. III. Influence of fertilization upon numbers of microorganisms in the soil. *In Soil Sci., v. 14,* p. 321-346.
- (59) WILSON, A. 1915 Changes in soil brought by heat. *In Proc. Roy. Dublin Soc., n. s., v. 38,* p. 513.

PLATE 1

INFLUENCE OF 1 PER CENT OF TOLUENE UPON THE FUNGOUS FLORA OF THE SOIL

The control jars are marked "c." The dilution for the toluene-treated pots was 10,000; for the controls, 1000.



INFLUENCE OF CALCIC AND MAGNESIC TREATMENTS UPON SULFATE LEACHINGS FROM SOIL ALONE AND WITH ADDI- TIONS OF FERROUS SULFATE, PYRITE, AND SULFUR

W. H. MACINTIRE, W. M. SHAW AND J. B. YOUNG

University of Tennessee Agricultural Experiment Station

Received for publication March 29, 1923

In a preliminary report (2) and a subsequent detailed contribution (6) upon the leaching of soil sulfates over an 8-year period, the influence of the oxides and carbonates of calcium and magnesium were shown to be divergent. That study had to do only with native materials, impurities of treatment, and rainfall, as sources of sulfates. Furthermore, the smallest additions were at the rate of 8 tons of CaO equivalence. It seemed desirable to ascertain whether added sulfureous materials are also subject to the divergent activities of calcium and magnesium. It was thought well to determine also the relative activities of economic applications of oxides and native carbonates upon soil without sulfur additions. Accordingly, in August, 1917, 3 years after the installation of the 46 lime-magnesia tanks, 22 additional lysimeters were placed. The sulfate leaching data secured from these 22 tanks during the first 5-year period are given in this contribution.

METHODS AND MATERIALS

While the annual periods for collection of leachings were from August to August, the annual rainfall collections were made quarterly. The 1917-1922 sulfate precipitations previously reported (5) are used in determining the amount of sulfate sulfur brought to the soil.

The tanks were filled August 2, 1917, with a loam soil designated as "Cherokee." It was acid to litmus and showed an electrometrically determined pH value of 6.27; ratio 1-10; one hour's contact. Sodium peroxide oxidation and disintegration showed an SO₃ content of 0.0815 per cent. One-foot tanks only were used, since the earlier work (2,6) had definitely established the function of the subsoil in changing the concentration of sulfate leachings under different conditions of treatment. The depth of soil in good tilth was about 8 inches. Each tank embraced an area of 1/20,000 acre and received 118.7 pounds of moist soil, equivalent to 100 pounds, moisture-free basis. The moist soil was screened, mixed and protected overnight during the determination of moisture upon a large sample. The alkali-earth treatments were all based upon equivalence of the designated number of pounds, or tons, of CaO per acre 2,000,000 pounds of moisture-free soil.

Three sulfur materials were used, ferrous sulfate, pyrite, and pulverized sulfur. These three materials carried 18.15 per cent, 51.95 per cent, and 99.89 per cent of sulfur, respectively. Each was applied in an amount equivalent to 1000 pounds of S per acre 2,000,000 pounds of soil. The combination afforded an opportunity for study of the outgo of sulfates from

a readily soluble application carrying the sulfate radical, as compared with pyrite, which upon oxidation yields the same soluble sulfate, plus SO₂, and the elementary form, without introducing any alkali addition. At the time of the inauguration of this experiment, insofar as known to us, no lysimeter investigation had been directed toward the availability of pyrite as a source of sulfur in soils. This material was included, therefore, as representing a cheap possible source of sulfur, in comparison with "flowers." The treatments are shown in the following outline:

Outline of calcium, magnesium, and sulfur additions

Tank No.	Treatment
50	Untreated soil
51	Ground limestone, 100-mesh, equivalent to 2,000 pounds CaO per acre
52	Ground dolomite, 100-mesh, equivalent to 2,000 pounds CaO per acre
53	Burnt lime, 2,000 pounds per acre
54	Burnt lime, 3,750 pounds per acre
55	Burnt magnesia, equivalent to 2,000 pounds CaO per acre
56	Burnt magnesia, equivalent to 3,750 pounds CaO per acre
57	FeSO ₄ , equivalent to 1,000 pounds of S per acre
58	FeSO ₄ , as in 57, and 3,750 pounds of CaO per acre
59	FeSO ₄ , as in 57, and MgO equivalent to 3,750 pounds of CaO per acre
60	FeSO ₄ , as in 57, and 32 tons of CaO per acre
61	FeSO ₄ , as in 57, and MgO equivalent to 32 tons of CaO per acre
62	FeS ₂ (pyrite), equivalent to 1,000 pounds of S per acre
63	FeS ₂ (pyrite), as in 62, and 3,750 pounds of CaO per acre
64	FeS ₂ (pyrite), as in 62, and MgO equivalent to 3,750 pounds of CaO per acre
65	FeS ₂ (pyrite), as in 62, and 32 tons of CaO per acre
66	FeS ₂ (pyrite), as in 62, and MgO equivalent to 32 tons of CaO per acre
67	Sulfur, 2,000 pounds S per acre
68	Sulfur, as in 67, and 3,750 pounds of CaO per acre
69	Sulfur, as in 67, and MgO equivalent to 3,750 pounds of CaO per acre
70	Sulfur, as in 67, and 32 tons of CaO per acre
71	Sulfur, as in 67, and MgO equivalent to 32 tons CaO per acre

It was planned to determine activation in sulfate generation through comparison between chemically equivalent amounts of limestone and dolomite at the rate ordinarily used in practice and a further joint comparison between these two materials and both burnt lime and magnesia upon the native sulfur materials in the soil. It was also intended to compare the effect of 1-ton and 32-ton admixtures of both CaO and MgO, where sulfur additions were made. The latter amount was taken as the maximum, in lieu of 100 tons, since the earlier work showed that the two heavy rates manifested the same tendencies. The limestone used was sulfur-free. The dolomite added sulfur at the rate of 35 pounds per 2,000,000 pounds of soil. The 2000-pound, 3750-pound, and 32-ton CaO additions showed impurities equivalent to 0.8 pound, 1.7 pounds, and 25.6 pounds, respectively. In the three corresponding additions of MgO the sulfur impurity amounted to 2.6 pounds, 4.9 pounds, and 83.2 pounds. Only the 25.6-pound impurity of the heavy CaO treatment and that of 83.2 pounds in the heavy MgO addition need be considered.

In order to have an actual supplement of 2000 pounds of CaO, it was necessary to take into account the immediate acidity of the FeSO₄ and also the potential acidity of the un-

oxidized sulfur materials. The 32-ton CaO and MgO treatments were sufficiently excessive to minimize the difference between immediate and potential acidity. The lime necessary to care for such acidity was therefore added as supplementary to the 2000-pound addition, making 3750 pounds, or its equivalent, the supplementary minimum for sulfur carriers.

TABLE 1

*First annual outgo of sulfates from Cherokee sandy loam—with and without sulfur additions—as influenced by calcic and magnesic materials**

TANK NUMBER	TREATMENTS PER 2,000,000 LBS. OF SOIL			TOTAL LEACHINGS liters	AVERAGE OF H_2SO_4 PER LITER FROM PERIODIC DETERMINATIONS gm.	S LOST IN LEACHINGS FROM AN ACRE SURFACE EXPOSURE, 2,000,000 LBS. OF SOIL							
	Calcic-magnesic		Equivalence of 1000 lbs. of S			Sept. 29, 1917	Jan. 29, 1918	Feb. 19, 1918	April 22, 1918	Aug. 3, 1918	Total 1917-1918		
	Material	CaO equivalence lbs. or tons				lbs.	lbs.	lbs.	lbs.	lbs.	lbs.		
50	None	None	None	85.70	0.0334	1.3	2.4	5.2	6.0	3.1	18.0		
51	Limestone	2000 lbs.	None	85.10	0.1128	9.0	7.9	14.2	21.8	4.9	57.8		
52	Dolomite	2000 lbs.	None	85.30	0.1230	8.5	9.9	15.0	23.3	5.5	62.2		
53	CaO	2000 lbs.	None	84.60	1223	8.3	9.3	15.9	22.9	5.8	62.2		
54	CaO	3750 lbs.	None	76.20	1812	10.5	13.6	23.2	26.2	7.1	80.6		
55	MgO	2000 lbs.	None	84.30	0.1398	9.7	10.6	14.5	21.2	6.7	62.7		
56	MgO	3750 lbs.	None	79.60	0.1936	13.7	11.0	32.6	29.3	7.0	93.6		
57	None	None	FeSO_4	75.21	3.0307	135.6	55.1	148.3	151.5	43.8	534.3		
58	CaO	3750 lbs.	FeSO_4	73.81	1.8867	138.3	82.7	236.8	300.5	71.1	829.4		
59	MgO	3750 lbs.	FeSO_4	71.52	2.7464	258.4	160.4	312.6	161.8	30.7	923.9		
60	CaO	32 tons	FeSO_4	77.70	0.1747	36.1	20.1	6.3	5.7	14.0	82.2		
61	MgO	32 tons	FeSO_4	54.93	3.3142	77.1	262.7	187.0	409.5	70.8	1007.1		
62	None	None	Pyrite	83.70	3661	14.7	23.7	53.6	80.2	25.1	197.3		
63	CaO	3750 lbs.	Pyrite	77.30	4025	25.6	19.3	40.9	69.0	34.5	189.3		
64	MgO	3750 lbs.	Pyrite	79.70	3989	27.3	29.9	25.3	76.6	24.5	183.6		
65	CaO	32 tons	Pyrite	84.40	0.0611	9.4	8.3	2.2	4.2	7.4	31.5		
66	MgO	32 tons	Pyrite	62.10	4258	11.5	27.6	39.1	71.0	16.3	165.5		
67	None	None	Sulfur	81.61	0.0504	55.4	69.8	149.4	188.9	43.3	506.8		
68	CaO	3750 lbs.	Sulfur	73.71	6422	96.9	66.2	195.2	287.4	87.8	733.5		
69	MgO	3750 lbs.	Sulfur	79.41	7062	101.3	204.6	160.2	284.0	66.5	816.6		
70	CaO	32 tons	Sulfur	88.50	0.1740	17.8	19.9	8.0	8.6	34.3	88.6		
71	MgO	32 tons	Sulfur	55.83	0.0761	28.4	76.9	0.0†	259.5	61.0	425.8		

* Rainfall—August to August 37.69 inches—S precipitated, 43.6 pounds.

† No leaching

It was difficult to anticipate the period required for oxidation of pyrite and sulfur; hence the possibility of a considerable difference between the amount of residual lime or magnesia in the tanks which received the 3750-pound basic treatment and the equivalence of free sulfuric acid and those which received the same basic supplement to the unoxidized sulfur

materials of potential acidity. Accordingly, such an experimental discrepancy was provided for by no-sulfur-addition controls which received lime and magnesia at the two rates of 2000 pounds and 3750 pounds.

In the earlier work where no sulfur was added, it was difficult to determine definitely whether the initial minimum and subsequent increase of sulfate leachings from heavy burnt lime additions were due to initial bacterial inhibition and subsequent recovery, or to depressed solubility of calcium sulfate as long as the soil water was impregnated with $\text{Ca}(\text{OH})_2$, or to physical and chemical changes in the soil as consequent to the conversion of the excess of hydrate to carbonate. It was hoped that the inclusion of ferrous sulfate would clarify this phase of the problem.

In the earlier investigation the effect of calcic and magnesian materials upon sulfur outgo was incidental to the main problem; hence, sulfate determinations were made only upon the annual composite of leachings. In the present study, however, the sulfate outgo was of primary interest, so that determinations of sulfates were made upon every periodic collection of leachings throughout the 5-year period. For the sake of brevity, the analytical results of tables 1-6 are expressed only as annual average BaSO_4 -per liter determinations and as pounds per acre for the separate leachings.

SULFATE LEACHINGS DURING THE FIRST YEAR

No-sulfur additions. Limestone and dolomite both caused a very decided increase in the leaching of sulfates in the several collections throughout the year. At the 1-ton rate, CaO and MgO gave practically identical yields; but at the 3750-pound rate, both oxides caused a heavier yield of soluble sulfates with the MgO giving greater response. These relationships held not only for annual outgo, but also for each of the 5 collections of drainage water. The 18-pound loss from the control was less than the 43.6-pound sulfur precipitation for the year, but the outgo from each of the 6 treatments was in excess of rainfall sulfur. It is therefore apparent that the treatments have either induced the passage of all, or much of the rain water sulfur, or they have generated additional sulfates from the sulfur materials in the soil, unless it be that they have forced out sulfates previously resistant to leaching.

FeSO_4 additions. The five collections from the sulfate control gave a total recovery slightly more than one-half of the FeSO_4 addition, as a result of the subnormal annual precipitation of 37.69 inches. Both supplementary treatments of CaO and MgO caused leachings very much heavier than those from the control, not only as totals, but also for all separate leachings, save one, the fifth and smallest. Eighty-one per cent of the addition is accounted for by the light CaO treatment and 91 per cent by the corresponding MgO treatment, after deducting the recovery obtained from the no-treatment control. An entirely different parallel appears, however, in the case of the 32-ton additions. Though added in soluble form at the beginning of the experiment, the sulfate addition did not come out in the leachings. The CaO so depressed the outgo of the incorporated soluble sulfate that the total for the year was only 10 per cent of that which came from the 1-ton plus supplement. This finding and similar results from the same lime supplement to the pyrite and sulfur treatments will be considered jointly in discussing chemical and

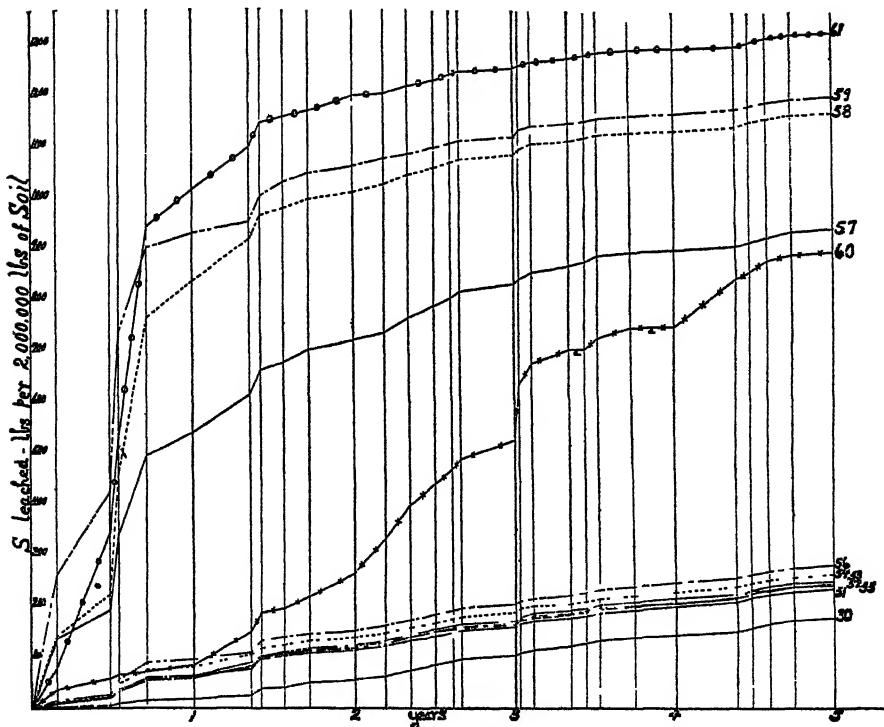


FIG. 1. INFLUENCE OF CaO, MgO, LIMESTONE AND DOLOMITE UPON LEACHING OF SULFATES DERIVED FROM SOIL AND RAINFALL AND RECOVERY OF ADDED FeSO₄, WITH AND WITHOUT CaO AND MgO, AS DETERMINED FROM PERIODIC LEACHINGS OVER A 5-YEAR INTERVAL

No sulfur

Tank 50, no supplement.

Tank 51, limestone, 2,000-lb. CaO equivalent.....

Tank 52, dolomite, 2,000 lb. CaO equivalent.....

Tank 53, CaO, 2,000 lbs..

Tank 54, CaO, 3,750 lbs..

Tank 55, MgO, 2,000-lb. CaO equivalent.....

Tank 56, MgO, 3,750-lb. CaO equivalent.....

Ferrous sulfate

Tank 57, no supplement.

Tank 58, CaO, 2,000 lbs. (+ 1750)

Tank 59, MgO, 2,000-lb. CaO equivalent (+ 1750)

Tank 60, CaO, 32 tons.....

Tank 61, MgO, 32-ton CaO equivalent.....

0-0-0-0

biochemical causes and in connection with previous work. On the other hand, the heavy MgO treatment was responsible for almost a full recovery, 98.91 per cent, of the added sulfate after deduction of the outgo from the no-treatment control.

Pyrite conditions. The control of this treatment gave an outgo which indicates an oxidation of 19 per cent of the addition. The reaction responsible for the oxidation of FeS_2 into FeSO_4 also generates SO_2 , equal quantities of S being accounted for by the two end-products. It is more probable that the

TABLE 2

*Second annual outgo of sulfates from Cherokee sandy loam—with and without sulfur additions—as influenced by calcic and magnesian materials**

TANK NUMBER	TREATMENTS PER 2,000,000 LBS. OF SOIL			TOTAL LEACHINGS liters	EQUIVALENCE OF 1000 LBS. OF S CaO EQUIVA- LENCE IN LBS. OR TONS	EQUIVALENCE OF BaSO_4 PER 1000 LBS. OF S AFTER FROM PERIODIC DETERMINATIONS	S LOST IN LEACHINGS FROM AN ACRE SURFACE EXPOSURE, 2,000,000 LBS. OF SOIL								
	Calcic-magnesian		Material				Dec. 11, 1918	Jan. 3, 1919	Feb. 24, 1919	April 22, 1919	Aug. 4, 1919	Total 1918-1919			
							lbs.	lbs.	lbs.	lbs.	lbs.	lbs.			
50	None	None	None	131.6	0.0444	8.4	11.7	1.8	9.7	5.6	37.2				
51	Limestone	2000 lbs.	None	130.5	0.0677	24.9	12.4	5.3	5.9	6.6	55.1				
52	Dolomite	2000 lbs.	None	130.9	0.0670	26.8	12.4	4.9	7.1	4.8	56.0				
53	CaO	2000 lbs.	None	131.1	0.0706	18.6	19.8	6.7	7.6	5.8	58.5				
54	CaO	3750 lbs.	None	122.3	0.0728	24.5	12.7	4.7	6.9	7.4	56.2				
55	MgO	2000 lbs.	None	124.4	0.0677	15.0	19.9	4.4	7.1	7.0	53.4				
56	MgO	3750 lbs.	None	124.9	0.0720	14.7	21.9	7.6	5.8	6.6	56.6				
57	None	None	FeSO_4	124.3	0.2249	67.9	54.1	14.7	25.7	18.5	180.9				
58	CaO	3750 lbs.	FeSO_4	121.7	0.2206	83.3	43.2	14.8	18.2	13.6	173.1				
59	MgO	3750 lbs.	FeSO_4	118.0	0.1783	22.3	50.7	24.3	18.1	13.8	129.2				
60	CaO	32 tons	FeSO_4	109.4	0.2839	66.7	35.9	8.7	22.0	45.1	178.4				
61	MgO	32 tons	FeSO_4	102.2	0.2133	84.8	46.6	10.6	10.9	31.0	183.9				
62	None	None	Pyrite	124.4	0.3407	139.2	64.4	5.6	36.7	32.9	278.8				
63	CaO	3750 lbs.	Pyrite	126.6	0.3115	151.1	42.4	4.6	19.1	45.9	263.1				
64	MgO	3750 lbs.	Pyrite	123.2	0.3123	149.1	36.9	19.7	11.9	37.0	254.6				
65	CaO	32 tons	Pyrite	132.0	0.0793	23.4	12.8	2.0	10.2	18.7	67.1				
66	MgO	32 tons	Pyrite	107.4	0.2315	43.2	33.5	14.3	9.5	6.7	107.2				
67	None	None	Sulfur	130.7	0.2504	80.6	67.7	19.8	26.0	16.9	211.0				
68	CaO	3750 lbs.	Sulfur	122.7	0.2977	121.9	64.6	15.6	19.1	14.5	235.7				
69	MgO	3750 lbs.	Sulfur	123.5	0.2708	137.8	37.9	13.5	15.0	14.4	218.6				
70	CaO	32 tons	Sulfur	122.9	0.2570	82.7	28.5	2.8	21.6	69.6	205.2				
71	MgO	32 tons	Sulfur	102.6	0.8640	395.4	154.2	26.1	18.9	12.9	607.5				

* Rainfall August to August 51.41 inches—S precipitated, 45.0 pounds.

moisture conditions of the soil and supplies of basic silicates, together with oxidative processes, are responsible for the conservation of the generated SO_2 as dissolved sulfates rather than permitting its loss in the gaseous phase. The-

inclusion of CaO and MgO at the 2000-pound-plus rate showed but little effect, 18 per cent oxidation having been indicated by the leachings from these two treatments. The additions of the two bases still further decrease the probability of loss of the SO₂ generated in the process of oxidation of FeS₂. The heavy CaO again showed distinct depressive influence upon sulfate outgo. The total recovery of 31.5 pounds was but little more than the loss from the no-sulfur control and less than the sulfur content of the annual precipitation. Indication of depressed oxidation is evidenced by the retardation of sulfate leachings from the heavy MgO addition, in comparison with the pyrite control and light treatments, and this indication finds substantiation in the still more striking results of the four succeeding years.

Sulfur additions. The sulfate sulfur outgo from the sulfur control was practically one-half of the amount introduced through treatment. Acceleration in outgo, as indicative of increased sulfification, was caused by the light treatments of both CaO and MgO, the latter having proved the more active. Once more the heavy burnt lime showed the smallest sulfate yield, although its leachings carried more than those from the same treatment used with either sulfate or pyrite and also five-fold more than the leachings from the no-treatment control. The heavy MgO addition gave a large recovery, though one considerably less than that of the sulfur control. It probably should be explained that the last leaching of the year from this treatment was very much smaller than the leachings from the other four tanks of the same group. There were no collections between August 4, the end of the first year, and December 11, when the first collections of the second year were obtained. This first collection of the second year was heavily impregnated with sulfates, carrying the per acre equivalent of 395.4 pounds of sulfate sulfur. When this amount is added to the total of the first year and the control is handled in the same way, an accelerative influence is shown for the heavy MgO addition.

SULFATE LEACHINGS DURING THE SECOND YEAR

No-sulfur additions. The loss from the control through leachings caused by the 51-inch rainfall was greater than that caused by the smaller and subnormal precipitation of the first year. The control outgo was still less than the content of rainfall and considerably less than the rather closely agreeing losses from the four 2000-pound and two 3750-pound calcic and magnesic additions.

FeSO₄ additions. The sulfate recovery from the FeSO₄ control was nearly the same as that from the light CaO treatment in spite of the large excess released by the latter during the first year. But the still greater excess initially shown by the light MgO was reflected in the decrease below that of the control. This tendency toward decrease was not manifested, however, by the heavy MgO addition. This may be due in part to activated oxidation of native materials and impurities, or accelerated movement of rainfall. The sulfate outgo from the heavy CaO was more than twice that of the initial year.

A decided decrease in $\text{Ca}(\text{OH})_2$ concentrations of leachings was also found. Nevertheless, a large fraction of the applied sulfate was still held back by the maximum CaO addition.

TABLE 3

*Third annual outgo of sulfates from Cherokee sandy loam—with and without sulfur additions—as influenced by calcic and magnesian materials**

TANK NUMBER	TREATMENTS PER 2,000,000 LBS. OF SOIL			TOTAL LEACHINGS liters	AVERAGE OF BaSO_4 PER LITER FROM PERIODIC DETERMINATIONS gm.	S LOST IN LEACHINGS FROM AN ACRE SURFACE EXPOSURE, 2,000,000 LBS. OF SOIL														
	Calcic-Magnesian		Equivalence of 1000 lbs. of S			Oct. 14, 1919		Dec. 8, 1919		Feb. 4, 1920		March 13, 1920		April 2, 1920		June 21, 1920†		Total 1919-1920		
	Material	CaO equivalence				lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.				
50	None	None	None	169.0	0.0450	6.5	12.4	8.7	7.2	5.3	6.5†					46.6				
51	Limestone	2000 lbs.	None	166.9	0.0426	8.4	9.6	8.4	6.5	4.4	6.2					43.5				
52	Dolomite	2000 lbs.	None	164.3	0.0453	8.0	11.2	9.4	6.8	4.4	5.7					45.5				
53	CaO	2000 lbs.	None	170.0	0.0460	10.2	11.4	9.1	7.0	4.1	6.5					47.8				
54	CaO	3750 lbs.	None	164.8	0.0490	10.0	8.7	9.2	7.4	4.8	8.8					48.9				
55	MgO	2000 lbs.	None	165.1	0.0462	9.6	11.0	9.9	6.5	3.6	6.2					46.8				
56	MgO	3750 lbs.	None	165.4	0.0508	10.5	10.7	9.5	7.3	5.0	8.3					51.3				
57	None	None	FeSO_4	165.2	0.1086	16.1	29.7	22.2	15.3	12.9	13.1					109.3				
58	CaO	3750 lbs.	FeSO_4	164.1	0.0745	17.0	18.5	13.3	9.1	7.5	8.8					74.2				
59	MgO	3750 lbs.	FeSO_4	160.3	0.0632	17.6	7.8	12.2	8.3	6.2	8.4					60.5				
60	CaO	32 tons	FeSO_4	127.6	0.3637	68.0	66.8	39.2	29.0	22.0	35.7					260.7				
61	MgO	32 tons	FeSO_4	136.4	0.0636	5.8	13.4	12.0	10.6	8.6	4.1					54.5				
62	None	None	Pyrite	162.3	0.2065	42.5	64.2	36.6	18.8	20.7	23.2					206.0				
63	CaO	3750 lbs.	Pyrite	164.7	0.1524	41.9	44.9	22.7	13.1	10.5	20.4					153.5				
64	MgO	3750 lbs.	Pyrite	165.3	0.1327	45.8	40.4	18.5	10.0	6.4	12.2					133.3				
65	CaO	32 tons	Pyrite	139.0	0.1216	21.0	20.4	14.3	12.4	9.8	18.6					96.5				
66	MgO	32 tons	Pyrite	139.5	0.0932	12.8	25.0	16.8	10.9	7.3	5.8					78.6				
67	None	None	Sulfur	167.2	0.1149	20.2	32.6	22.8	13.6	12.7	15.6					117.5				
68	CaO	3750 lbs.	Sulfur	160.7	0.0797	17.0	21.5	15.0	9.3	7.4	7.9					78.1				
69	MgO	3750 lbs.	Sulfur	162.1	0.0712	17.8	17.9	12.9	8.3	5.5	8.0					70.4				
70	CaO	32 tons	Sulfur	145.1	0.3175	73.9	65.8	30.4	23.7	21.7	47.6					263.1				
71	MgO	32 tons	Sulfur	143.1	0.1335	30.9	37.0	22.7	13.3	8.1	5.4					117.4				

* Rainfall—August to August 54.75 inches—S precipitated, 44.1 pounds.

† No leaching between June 21 and close of annual period August 4.

Pyrite additions. The same order of sulfur recoveries obtained as for the previous year. Slight retardation in oxidation was evidenced by the sulfate outgo from the two oxides in light applications, with more decided indication

in the heavy MgO treatment and still greater repression for the heavy addition of burnt lime. The yield of 67.1 pounds in this last instance, however, was more than double that from the same tank during the previous year. Very much heavier recoveries were obtained from the heavy CaO treatment where sulfur was supplied as sulfates and where derived from oxidation of added elementary sulfur. Since the recovery of added sulfate was increased by light treatments of both CaO and MgO, it is apparent that the oxidation of the pyrite was not accelerated by the light additions of either lime or magnesia, while it was distinctly depressed by the heavier treatments of both materials.

Sulfur additions. The sulfate recovery from each of the light additions was greater than that from the control, although the latter contained a considerably larger residue as a result of the greater losses from the CaO and MgO during the first year. All of the treatments yielded greater quantities of sulfates than those which came from the same treatments in the FeSO₄ group during the second year. But, even with smaller unoxidized residues from additions, the yield from each treatment in the sulfur group was more than that from the corresponding alkali-earth supplement in the pyrite group. Coincident with removal of excess of hydrate through leaching and through carbonation, the repressive influence of the heavy CaO addition was materially lessened. The large outgo of 607.5 pounds of sulfate sulfur from the heavy MgO treatment is accounted for by the fact that the sulfate content of the first leaching of the second year was about equivalent to the aggregate sulfate outgo of the first year and about two-thirds of the total outgo of the second year. As stated, this initial leaching of the second year came after an unusually dry spell, which extended from August to December.

OUTGO OF SULFATE DURING THE THIRD YEAR

No-sulfur additions. The sulfates passing from the control slightly exceeded the losses from the limestone and dolomite treatments and were almost equal to those from the 1-ton and 3750-pound additions of CaO and MgO, and for the first time equaled the amount brought down by rain.

FeSO₄ additions. The leachings from the FeSO₄ control carried more sulfates than did those of either of the light additions, and also more than those of the heavy MgO treatment. The outgo from the heavy lime incorporation was the maximum for the group and the largest of the progressive increases in annual losses from the same tank during the first three years. The parallel of Ca(OH)₂ reversion to carbonate and the progressive tendency of the soil to release added, or engendered, sulfates is again indicated. After recovery in excess of the addition, as a result of the extensive leaching of the first year, and the considerable yield for the second year, the heavy MgO dropped during this year to an outgo close to that of the control. Because of the readiness with which the magnesium salts are removed by leaching, it is probable that the sulfate outgo from the heavy addition of magnesium oxide was derived mainly

from the sulfate addition and rainfall rather than from sulfates engendered from components native to the soil.

TABLE 4

*Fourth annual outgo of sulfates from Cherokee sandy loam—with and without sulfur additions—as influenced by calcic and magnesian materials.**

TANK NUMBER	TREATMENTS PER 2,000,000 LBS. OF SOIL			TOTAL LEACHINGS gm.	S LOST IN LEACHINGS FROM AN ACPE SURFACE EXPOSURE, 2,000,000 LBS. OF SOIL								Total 1920-1921 lbs.		
	Calcic-magnesian		Equivalence of 1000 lbs. of S		AVERAGE OF BaSO ₄ PER LITER FROM PERIODIC DETERMINATIONS		Aug. 14, 1920	Sept. 10, 1920	Dec. 8, 1920	Jan. 10, 1921	Feb. 10, 1921	April 23, 1921	Aug. 4, 1921		
	Material	CuO equiv- lence			lbs.	lbs.									
50	None	None	None	187.8	0.0357	4.7	6.9	6.3	6.5	6.2	5.2	4.7	4.7	40.5	
51	Lime-stone	2000 lbs.	None	192.1	0.0349	5.6	6.8	5.1	5.1	5.6	5.8	6.7	6.7	40.7	
52	Dolomite	2000 lbs.	None	193.5	0.0349	5.2	6.3	5.6	5.2	5.7	6.6	6.3	40.9		
53	CaO	2000 lbs.	None	190.1	0.0393	7.7	7.5	5.2	5.4	6.2	6.5	6.6	45.1		
54	CaO	3750 lbs.	None	178.3	0.0379	7.3	5.0	4.4	5.0	6.4	5.7	6.4	40.2		
55	MgO	2000 lbs.	None	182.1	0.0386	8.0	7.3	5.4	5.0	5.9	5.6	5.5	42.7		
56	MgO	3750 lbs.	None	181.0	0.0400	6.6	5.3	6.0	5.1	5.6	6.4	8.0	43.0		
57	None	None	FeSO ₄	176.5	0.0626	9.6	14.3	12.0	8.8	10.1	7.8	5.1	67.7		
58	CaO	3750 lbs.	FeSO ₄	178.9	0.0451	11.3	10.8	7.3	5.6	5.2	5.0	5.0	50.2		
59	MgO	3750 lbs.	FeSO ₄	175.5	0.0429	10.1	9.3	5.5	5.2	5.9	4.9	5.1	46.0		
60	CaO	32 tons	FeSO ₄	120.5	0.3232	107.9	42.5	26.9	†	23.0	21.1	†	221.4		
61	MgO	32 tons	FeSO ₄	165.8	0.0400	6.7	6.8	7.5	6.3	5.7	4.9	3.5	41.4		
62	None	None	Pyrite	178.2	0.1055	16.6	23.9	22.3	15.3	17.2	12.5	8.2	116.0		
63	CaO	3750 lbs.	Pyrite	180.8	0.1106	25.2	16.3	16.7	12.9	12.7	14.8	21.1	119.7		
64	MgO	3750 lbs.	Pyrite	180.4	0.0772	17.7	17.3	12.2	8.1	18.7	7.8	12.5	94.3		
65	CaO	32 tons	Pyrite	156.1	0.1507	29.3	15.8	19.3	11.8	12.2	11.0	32.5	131.9		
66	MgO	32 tons	Pyrite	163.6	0.0539	9.4	10.4	10.6	9.1	6.5	4.6	3.7	54.3		
67	None	None	Sulfur	180.1	0.0633	8.6	16.3	13.5	8.5	10.8	8.4	3.9	70.0		
68	CaO	3750 lbs.	Sulfur	176.4	0.0466	12.3	11.4	6.8	5.2	6.1	5.4	3.9	51.1		
69	MgO	3750 lbs.	Sulfur	176.4	0.0459	10.1	8.7	7.2	6.2	6.3	5.5	5.6	49.6		
70	CaO	32 tons	Sulfur	164.5	0.2344	57.4	26.7	29.5	18.5	16.5	20.4	48.7	217.7		
71	MgO	32 tons	Sulfur	161.4	0.0524	7.3	9.5	11.2	8.5	6.6	4.7	3.3	51.1		

* Rainfall, August to August 55.19 inches; S precipitated, 44.0 pounds.

† No leaching.

Pyrite additions. The pyrite control continued to liberate more sulfates to the leachings than did either of the light amendments. The heavy additions of both lime and magnesia still further depressed the sulfate liberation, the

magnesia being the more depressive for both rates. It is apparent that the larger amount of magnesia is very much more depressive upon the agencies responsible for the oxidation of pyrite than upon those responsible for the conversion of elementary sulfur into sulfates.

Sulfur additions. After exceeding the control in sulfate losses during the first two years, both light basic treatments trailed in outgo of sulfates during the third year. At the beginning of the third year the heavy MgO treatment had already caused a sulfate sulfur outgo in excess of the amount of elementary sulfur added. The sulfate leaching for the third year, therefore, suffered a decided decrease, though it was still equal to the loss from the sulfur control. It was also $2\frac{1}{2}$ times as great as the outgo from the no-treatment control and more than twice as great as rainfall sulfur. The heavy lime treatment acted as a deterrent, as it did when used with the soluble FeSO₄. After progressive increases the maximum outgo occurred during the third year.

Although inhibitive to nitrification during the period of the first four leachings of the initial year, the 32-ton lime treatment distinctly accelerated the nitrate outgo during the leachings of the fifth collection and it has continued to do so during the rest of the five years. Therefore, without amplification of these results, it is not proved that sulfates were not formed biologically from the elementary sulfur added with the heavy treatment of lime, even though such sulfates did not appear in the leachings in amounts so large as those in other treatments of the same group.

OUTGO OF SULFATES DURING THE FOURTH YEAR

No-sulfur additions. The sulfate loss from the control was almost identical with losses from both native carbonates and the loss from the 3750-pound CaO treatment. It was but little less than the losses from the three other treatments of lime and magnesia in this group.

FeSO₄ additions. The outgo from this control continued in the direction of progressive decrease from the maximum of the initial year. The light lime treatment and both light and heavy magnesia additions showed the same tendency. The recovery from each of these three treatments was less than the loss from the control, as had been the case during the second and third years, following excessive amounts of the first year. The outgo from the heavy CaO was very much greater than that from any of the other four tanks of the groups. The peak of the sulfate outgo from the heavy lime addition had been reached, however, during the previous year and the loss during the fourth year represents an intermediate step between the outgo of the third year and that of the fifth year, in progressive recession from the maximum.

Pyrite additions. The recovery from the control and that from the light CaO supplement were in close agreement. Both recoveries showed positive progressive decrease from corresponding maximum losses of the second year. The same was true of the somewhat smaller outgo from the 3750-pound

MgO addition. A still smaller recovery, the smallest of the pyrite group, came from the heavy MgO treatment, and maintained the progressive order of decrease from the maximum of the initial year. This order of outgo was the same as that maintained by the added soluble sulfate. The largest recovery

TABLE 5

*Fifth annual outgo of sulfates from Cherokee sandy loam—with and without sulfur additions—as influenced by calcic acid and magnesian materials**

TANK NUMBER	TREATMENTS PER 2,000,000 LBS. OF SOIL			TOTAL LEACHINGS 1000 lbs. of S	AVERAGE OF FeSO_4 PER LITER FROM PERIODIC DETERMINATIONS	S LOST IN LEACHINGS FROM AN ACRE SURFACE EXPOSURE, 2,000,000 LBS. OF SOIL							
	Calcic-magnesian												
	Material	CaO equivalence lbs. or tons	Equivalence of 1000 lbs. of S			Dec. 20, 1921 gm.	Jan. 21, 1922 lbs.	Mar. 2, 1922 lbs.	April 28, 1922 lbs.	Aug. 3, 1922 lbs.	Total 1921-1922 lbs.		
50	None	None	None	142.3	0.0386	5.5	8.1	8.3	7.0	4.6	33.5		
51	Limestone	2000 lbs.	None	139.2	0.0415	8.6	9.1	5.5	6.1	5.5	34.8		
52	Dolomite	2000 lbs.	None	139.2	0.0444	8.6	10.0	7.9	5.9	4.8	37.2		
53	CaO	2000 lbs.	None	133.2	0.0429	8.3	7.8	7.4	5.9	4.8	34.2		
54	CaO	3750 lbs.	None	132.7	0.0437	10.1	7.4	6.8	5.0	5.4	34.7		
55	MgO	2000 lbs.	None	135.0	0.0429	9.2	8.4	6.7	5.9	4.7	34.9		
56	MgO	3750 lbs.	None	138.4	0.0408	8.9	6.4	7.6	5.6	5.3	33.8		
57	None	None	FeSO_4	124.6	0.0560	5.8	9.2	10.1	9.8	7.5	42.4		
58	CaO	3750 lbs.	FeSO_4	130.2	0.0473	8.2	8.9	8.0	6.2	6.2	37.5		
59	MgO	3750 lbs.	FeSO_4	128.6	0.0473	8.4	9.1	7.2	6.3	5.5	36.5		
60	CaO	32 tons	FeSO_4	110.9	0.2402	95.2	19.4	15.7	10.5	6.4	147.2		
61	MgO	32 tons	FeSO_4	107.1	0.0510	4.3	8.8	11.4	6.6	3.2	34.3		
62	None	None	Pyrite	132.3	0.1077	18.7	18.8	19.8	16.8	12.5	86.6		
63	CaO	3750 lbs.	Pyrite	132.4	0.1136	29.1	20.0	15.1	13.7	13.9	91.8		
64	MgO	3750 lbs.	Pyrite	133.4	0.0699	18.7	12.2	8.4	8.5	7.9	55.7		
65	CaO	32 tons	Pyrite	108.6	0.1405	38.8	14.3	11.4	8.2	14.0	86.7		
66	MgO	32 tons	Pyrite	111.2	0.0713	8.7	14.4	14.8	7.8	4.2	49.9		
67	None	None	Sulfur	137.5	0.0611	8.9	11.6	11.5	10.7	7.6	50.3		
68	CaO	3750 lbs.	Sulfur	132.7	0.0473	8.8	9.4	7.7	6.6	5.3	37.8		
69	MgO	3750 lbs.	Sulfur	134.4	0.0459	9.8	9.7	6.9	5.4	5.2	37.0		
70	CaO	32 tons	Sulfur	112.2	0.1827	76.2	17.3	9.6	6.3	7.6	117.0		
71	MgO	32 tons	Sulfur	104.5	0.0575	5.7	9.8	11.5	6.9	3.5	37.4		

* Rainfall, August to August 56.75 inches; S precipitated 38.0 pounds.

came from the heavy CaO admixture and represented the maximum up to this time in the progressive increases from the minimum of the initial year.

Sulfur additions. The sulfate recoveries from the three additions, light CaO and both light and heavy MgO, were practically identical and consider-

ably less than the outgo from the control. The two lighter treatments and the control gave up sulfates in amounts which placed them in the position of showing the third successive drop in the progressive decrease from maxima of the initial year, being parallel in this respect to their effect when used in connection with the additions of the soluble sulfate. The heavy MgO gave a sulfate return in similar progressive decrease from the maximum of the second year. The maximum for this treatment came in the second year rather than in the first, because of the previously mentioned repressed leaching as a result of marked influence upon the physical characteristics of the soil. The heaviest yield of the year came from the burnt lime, which was also the case in the other two groups which received sulfur carriers. This was the second largest recovery of the 5-year period, corresponding in that regard to the return induced by the same treatment when used in conjunction with the soluble sulfate of iron.

OUTGO OF SULFATES DURING THE FIFTH YEAR

No-sulfur additions. The losses from the control, the two lime, the two magnesia, and the two limestone additions were in close agreement, and each outgo was less than the amount of sulfate sulfur brought down by rainfall. These concordant losses corresponded in general to those from the soluble sulfate additions and those from the elementary sulfur additions, except where the heavy amount of lime was added to the two forms. They were still appreciably less, however, than the several recoveries from the pyrite for the fifth year.

FeSO₄ additions. The amounts of sulfate sulfur given up by the light lime and both light and heavy MgO were nearly the same and somewhat less than the amount derived from the ferrous-sulfate control. Each yield represented, respectively, the minimum outgo from the several joint treatments over the 5-year period. The leachings from the heavy addition of burnt lime carried the largest sulfate yield derived during the year from the iron sulfate group. This outgo of 147.2 pounds of marked the second drop in annual outgo from the 260.7-pound maximum of the third year.

Pyrite additions. As compared with the several recoveries of the preceding year, all pyrite additions showed decreases in outgo. With the exception of that from the heavy burnt lime, each recovery for the year represented the minimum outgo for the 5-year period. The sulfates released to the leachings by the 32-ton burnt-lime addition constituted the heaviest return from the sulfur group during the year.

Sulfur additions. In harmony with the recoveries from the sulfate group, those from the two light oxide additions and the 32-ton treatment were practically identical, equivalent to rainfall sulfates and less than the recovery from the elementary sulfur control. Each of these four recoveries represented, respectively, the minimum annual outgo from the several combinations for the 5-year period. The heavy CaO gave the largest recovery of the sulfur group

for this year. However, as was true also of the sulfate, group, the fifth annual outgo from the heavy burnt lime was next to the smallest of the 5-year period. In the case of the heavy CaO supplements, both groups showed the decreasing order in outgo for third, fourth, second, fifth, and first years.

TABLE 6

Summary of leaching data from 256 inches precipitation for the 5-year period and calculation of total loss in per cent of sulfur content of soil, sulfur additions and rainfall

TANK NUMBER	TREATMENT PER 2,000,000 LBS. OF SOIL			LEACHING DATA FOR 5-YEAR PERIOD								
	Calcic — magnesic		Equivalent of 1000 lbs. of S	Total volume leached	Average BaSO ₄ per liter	Total sulfate-sulfur outgo as					Excess per acre	
	Material	CaO equivalent lbs. or tons				S per 2,000,000 lbs. of soil	per cent	Fraction of initial sulfur content of soil	Fraction of sulfur applied	Related to sulfur in rainfall	lbs.	
50	None	None	None	716.4	0.0394	175.8	10.8			81.9	-38.9	
51	Limestone	2000 lbs.	None	713.8	0.0599	321.9	14.2			108.0	17.2	56.1
52	Dolomite	2000 lbs.	None	713.2	0.0629	241.8	14.8			112.6	27.1	66.0
53	CaO	2000 lbs.	None	709.0	0.0642	247.8	15.2			115.4	33.1	72.0
54	CaO	3750 lbs.	None	674.3	0.0769	260.6	16.0			121.4	45.9	84.8
55	MgO	2000 lbs.	None	690.9	0.0670	240.5	14.8			112.0	25.8	64.7
56	MgO	3750 lbs.	None	689.3	0.0795	278.5	17.1			129.7	63.8	102.7
57	None	None	FeSO ₄	665.8	0.3512	934.6	57.3	93.5	435.3	719.9	758.8	
58	CaO	3750 lbs.	FeSO ₄	668.7	0.4548	1164.4	71.4	116.4	542.3	949.7	988.6	
59	MgO	3750 lbs.	FeSO ₄	653.9	0.6156	1196.1	73.4	119.6	557.1	981.4	1020.3	
60	CaO	32 tons	FeSO ₄	546.1	0.2771	889.9	54.6	89.0	414.5	675.2	714.1	
61	MgO	32 tons	FeSO ₄	566.4	0.7364	1321.2	81.1	132.1	615.3	1106.5	1145.4	
62	None	None	Pyrite	681.4	0.2253	884.7	54.3	88.5	412.1	670.0	708.9	
63	CaO	3750 lbs.	Pyrite	681.4	0.2181	817.4	50.1	81.7	385.2	602.7	641.6	
64	MgO	3750 lbs.	Pyrite	687.0	0.1982	721.5	44.3	72.2	336.1	506.8	545.7	
65	CaO	32 tons	Pyrite	620.1	0.1106	413.7	25.4	41.4	192.7	199.0	237.9	
66	MgO	32 tons	Pyrite	583.8	0.1751	455.5	27.9	45.6	212.2	240.8	279.7	
67	None	None	Sulfur	697.1	0.3080	955.6	58.6	95.6	445.1	740.9	779.8	
68	CaO	3750 lbs.	Sulfur	666.2	0.4227	1136.2	69.7	113.6	529.2	921.5	960.4	
69	MgO	3750 lbs.	Sulfur	675.8	0.4280	1192.2	73.1	119.2	555.3	977.5	1016.4	
70	CaO	32 tons	Sulfur	633.2	0.2331	891.6	54.7	89.2	415.2	676.9	715.8	
71	MgO	32 tons	Sulfur	567.4	0.8367	1239.2	76.0	123.9	577.2	1024.5	1063.4	

TOTAL SULFATE LOSSES DURING THE 5-YEAR PERIOD

Table 6 gives the totals of leaching volumes and sulfur losses for the 5-year period and the grand averages of BaSO₄-per-liter determinations.

Volumes of leachings. Space forbids a full discussion of the influence of treatment upon the volumes of leachings from rainfall, for such a discussion would involve a detailed consideration of variation in soil bulk due to treatment and of periodicity of precipitation. It is sufficient to point out one or two relationships. The differences between the leaching from the control and the leachings from the two limestone additions are negligible, since no secondary effect of residues from enhanced plant growth is involved. Both lime treatments and both magnesia additions, however, yielded leaching volumes somewhat smaller than those of the control. All of the FeSO₄ additions gave collections considerably below those of the control and also light amendment treatments. Considerable diminution in leaching volumes was caused by the heavy additions used in connection with the three sulfur carriers. This effect was probably due in part to the larger resultant mass, as well as to amelioration in physical condition. In spite of decreased leaching volumes, the large applications of burnt lime produced a seemingly dry granular soil which must have retained far more moisture than that indicated by its physical condition. The magnesia, however, produced a somewhat sticky condition and the soil apparently retained the excess of moisture in a different manner than that treated with burnt-lime.

The data in the sixth column of table 6 show the average of BaSO₄ determinations on the liter basis, from which may be seen the material analytical differences obtained.

No-sulfur additions. The aggregate loss of sulfates from the control was equivalent to 10.8 per cent of the soil's initial content of sulfur. There was a conservation of 38.9 pounds, or 18.1 per cent, of the precipitated sulfates for the 5-year period. The passage of rainfall sulfur through this soil amounted to 81.9 per cent of the precipitation, as compared with 69 per cent in the case of the control of the previously reported 8-year experiment.

The total losses from the limestone and dolomite treatments were rather close, the dolomite having given an average annual yield of 2 pounds more than the limestone. The 10-pound excess for the period was equivalent to about one-third of the amount of sulfur carried by the sphalerite or other sulfur materials in the dolomite. The differences between sulfate sulfur leachings and the total 5-year precipitation of sulfate sulfur—214.7 pounds—give total actual sulfate losses of 17.2, 27.1, 33.1, 45.9, 25.8, and 63.8 pounds, respectively, for tanks 51 to 56 inclusive. These excesses of outgo above sulfur income are equivalent, respectively, to annual losses of 3.4, 5.4, 6.6, 9.2, 5.2, and 12.8 pounds. The 6 tanks 51–56 show losses in excess of the control outgo varying from 56.1 pounds to 102.7 pounds.

FeSO₄ additions. The addition of soluble ferrous sulfate, unsupplemented, gave a recovery of 934.6 pounds of sulfate sulfur from the 1000-pound application. When the rainfall sulfur is subtracted from this, a recovery of 719.9 pounds, or 71.99 per cent, of the sulfate treatment is accounted for. The difference between the outgo from the FeSO₄ and no-treatment controls gives an actual yield of 758.8 pounds. Since the recovery of the fifth year was only 50.3 pounds, as against a 33.5-pound loss from the control and 38.0 pounds from rainfall it is most probable that years will be required to equalize the disparity of 280.1 pounds if such is still in the acid soil.

It was interesting to observe that no ferrous sulfate ever appeared in the leachings, every one of which was free of iron and alkaline to methyl orange. The FeSO₄ was neutralized by the silicates of the acid soil, for increase in sulfate content of the leachings was accounted for in the main by increases in calcium and magnesium content. This is not in harmony with the viewpoint of Van Bemmelen (9), cited by Rudolfs (8), to the effect that sulfuric acid generated in the soil is more active upon the iron oxide than upon silicates of the soil, as set forth by the quotation "the iron oxide in the soil protects, to a certain extent, the humate and silicate bases against the action of sulfuric acid.

Assuming continued occurrence of the unrecovered fraction of the applied soluble sulfate it seems hardly probable that this unaccounted-for difference could be held in original form or as basic sulfates in the *acid* soil with such tenacity as to resist the solvent action of the repeated leachings. But the factors of ample drainage and optimum aeration do not favor the assumption of de-sulfification. However, this alternative finds some support from the fact that the acid soil control gave a decidedly lower recovery than was obtained from the alkaline conditions other than that induced by the heavy burnt lime. It is possible, however, that some of the soluble added sulfates may have resulted in the formation of insoluble sulfates in the soil.

The 1750-pound excesses above the 2000-pound alkali-earth treatments intended to insure the immediate conversion of the acid sulfate to calcium or magnesium sulfate, were responsible for decided increases in leached sulfates. The two treatments of CaO and MgO were responsible, respectively for sulfur yields of 1164.4 pounds and 1196.1 pounds, or recoveries of 94.97 per cent and 98.14 per cent, after deduction of the increment from rain water and corresponding yields of 988.6 pounds and 1020.3 pounds after deducting the outgo from the untreated control. The heavy addition of MgO was responsible for a still greater and a much quicker passage of sulfates. Of the total of 1321.2 pounds for the 5-year period 1007.1 pounds were recovered from the five leachings of the first year and 183.9 pounds from the six leachings of the second year. After deduction of the income from rainfall sulfur, an outgo of 106.5 pounds in excess of the amount added was obtained. Deducting the 175.8-pound loss from the no-treatment control, an actual outgo of 1145.4 pounds, or 145.4 pounds in excess of addition was obtained. These excesses

necessarily were derived from the sulfur content of the soil or in part from alkali-earth-treatment impurities.

The heavy burnt-lime treatment exhibited a distinct retardation in the outward movement of sulfates. This repressive tendency was most effective

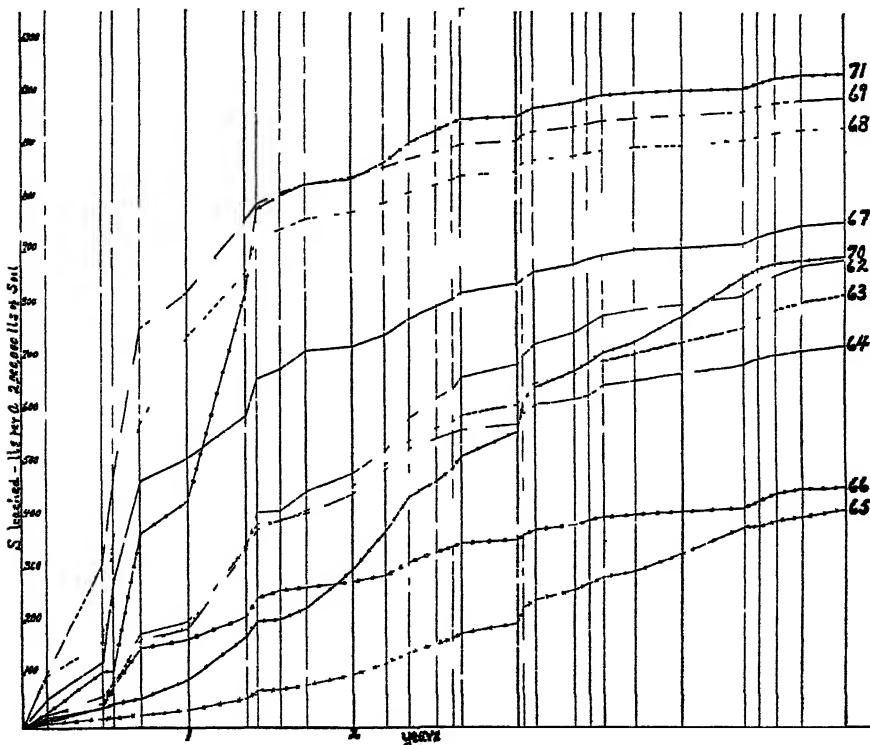


FIG. 2. INFLUENCE OF CaO AND MgO UPON LEACHINGS OF SULFATES DERIVED FROM PYRITE AND FLOWERS OF SULFUR, AS DETERMINED FROM PERIODIC LEACHINGS OVER A 5-YEAR INTERVAL

	<i>Pyrite</i>	<i>Sulfur</i>
Tank 62.	No supplement	Tank 67.....
Tank 63.....	- - - - CaO, 2,000 lbs. (+ 1750)	Tank 68.....
Tank 64.....	- - - - MgO, 2,000 lb. CaO equivalent (+ 1750)	Tank 69.....
Tank 65	x-x-x-x-x CaO, 32 tons	Tank 70.....
Tank 66.....	o-o-o-o-o MgO, 32-ton CaO equivalent	Tank 71.....

during the first year. The outgo for the second year was more than twice that of the initial year, while the maximum annual leaching came during the third year. Each of the five leachings of the first year contained $\text{Ca}(\text{OH})_2$, the average normality having been 0.00654, within a range between a maximum of

0.0158 normal to a minimum of 0.0005 normal. The same held true for the first three of the five leachings of the second year, which showed an average normality of 0.00157, with extremes of 0.00225 and 0.0008. Even the third, fourth, and fifth of the six leachings of the third year showed alkalinity ranging between 0.000075 and 0.000425 normal. Previous data (6) demonstrated that with conditions optimum for saturation, these concentrations are not sufficiently repressive in solvent action upon CaSO_4 to account for the lesser outgo of sulfates from the soil which received the heavy lime additions. The CaO treatment has either transformed the added sulfate into less soluble combinations, or it has so materially ameliorated the soil as to increase decidedly its ability to retain the CaSO_4 , which must have been formed as a result of the thorough dissemination of the large excess of alkali-earth. From considerable supplementary work already done it is believed that this phase of the problem will be clarified.

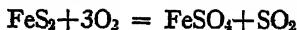
Pyrite additions. It is commonly observed that pyrite oxidizes during the disintegration of exposed minerals carrying it as impurities. The mineral was included in parallel with elementary sulfur in order to determine its activity in the soil, with the thought that the sulfates derived therefrom would be furnished more gradually than from sulfur "flowers" or powder.

In a preliminary report upon related laboratory studies growing out of the use of pyrite in the soil of the 1917 installation of lysimeters, reference to the sulfate content of leachings was made (3):

The data secured demonstrated that the flowers of sulfur and iron pyrite were both converted into sulfates with distinct rapidity.

It was first assumed that the oxidation of both the elementary sulfur and that of the pyrites was induced in the main, if not solely, by organisms. However, some doubt concerning this assumption was introduced about 2 yrs. after the inauguration of the experiment, when it was observed that a strong odor of sulfur dioxide was given off from the reserve sample of iron pyrites, which had been kept in the dark in an 8-oz. glass bottle, tightly stoppered with an ordinary No. 6 cork stopper. A 10-g. charge of the pyrites was found to yield soluble sulfate of iron equivalent to a determined weight of 0.4172 g. of BaSO_4 , as an average of seven determinations. The same observation has been reported by Allen and Johnston.

These investigators accounted for the oxidation by means of the equation:



They also found that the grinding of pyrite and marcasite for 1-hour and 6-hour periods was responsible for decided increases in sulfate generation. The rapidity and extent of this result were so marked as to preclude the probability of bacterial activities, as against the probability of chemical activation through frictional heat and increase of surface. In September, 1919, Mr. F. J. Gray formerly of this laboratory staff, conducted an adjunct laboratory experiment, using the same soil, materials, and amounts, in an effort to differentiate between chemical and biochemical agencies responsible for the oxidation of pyrite and also elementary sulfur under dry and optimum moisture conditions. These results have been held for publication, as supplementary to

those of the parent lysimeter investigation. They show that the oxidation is brought about by both chemical and biochemical agencies.

The sulfate leachings are of interest in their connection with the results of Rudolfs (7), who has recently reported studies which dealt with the activities of bacteria in oxidizing pyrite. In the paper upon bacterial oxidation of pyrite no mention was made by Rudolfs of our related lysimeter results (3, 4) reported under captions which referred only to elementary sulfur. In a later contribution Rudolfs (8) referred to one of the two preliminary papers (4), as to chemical oxidation of elementary sulfur, but apparently overlooked our assumption that bacterial activities to some extent accounted for the recovery of sulfates in the leachings from pyrite.

While it is undoubtedly true, as pointed out by Rudolfs (7), that bacteria can and do convert the FeS_2 of pyrite into sulfates in soil media, it is also apparent that the inherent oxidative properties and moisture conditions of the soil serve to accelerate the purely chemical oxidative reactions which transpire even in air-dry condition in the atmosphere.

The sulfur recoveries from the pyrite group do not show the same order which obtained in the ferrous sulfate group. The maximum sulfur recovery, as sulfates leached from the pyrite additions, was obtained from the acid soil, in which respect this control differed from the controls of the other two sulfur-addition groups. A distinct retardation was caused by the light lime treatment, while the light MgO addition was even more effective in the same direction. This relationship between the three totals for the 5-year period was consistently maintained between the respective annual losses of the first three years, which gave the three largest losses in each case, the outgo of the second year having been the maximum for each of the three conditions. The heavy additions of CaO and MgO were both still more decidedly depressive upon sulfate generation, if the repressive influence of outgo and depressed generation be considered as identical. It will be observed that the heavy CaO addition occupied the same relative position, that of minimum, as in both the FeSO_4 and elementary sulfur groups. This was not the case, however, with the MgO , which caused the maximum sulfate outgo from the sulfur additions of the other two groups. Furthermore, the heavy burnt-lime addition increased progressively from the minimum of the initial year to the maximum of the fourth year. This progressive increase followed a progressive decrease in $\text{Ca}(\text{OH})_2$ concentrations in the leachings. Calcium hydroxide was present in all of the five collections of the first year, in all five of those of the second year, and in four of the six of the third year. The average of $\text{Ca}(\text{OH})_2$ concentrations of leachings for the three years were 0.01327 N., 0.001255 N., and 0.00055 N., in order. On the other hand, the corresponding MgO addition gave its maximum sulfate outgo during the first year, with progressive decreases to its minimum in the fifth year. In this regard, the heavy MgO treatment acted as it did in the other two groups. The heavy lime treatment also showed somewhat the same tendency as in the other two

sulfur-addition groups. It is apparent that the influences of the excessive additions of both oxides were very much more depressive to the chemical or biochemical, or both, reactions responsible for the oxidation of FeS_2 , than to the reactions which convert sulfur into sulfates. However, even assuming that all precipitated sulfates were leached through the soil, deducting such from the total leachings, and assuming no sulfates to have been derived from the organic matter of the soil or basic treatment, we find that 67.0 per cent of the added FeS_2 has been converted into sulfates in the acid control. With the same assumptions, we find recoveries of 60.3 per cent and 50.7 per cent from the light treatments of CaO and MgO , respectively, and 19.9 per cent and 24.1 per cent from the two heavy additions. Thus, in the case of the lighter treatments, MgO was more retardative than CaO upon the outgo of sulfates, while the reverse was true for the heavy additions. Applying the 175.8-pound outgo from the untreated control as a corrective factor to the sulfate leachings from the five pyrite tanks, 64.16 per cent and 54.57 per cent recoveries came from light CaO and MgO , respectively, as compared with 70.89 per cent from the sulfate control, while the two heavier oxide treatments gave corresponding recoveries of only 23.79 per cent and 27.97 per cent.

Sulfur additions. The sulfate yields from the elementary sulfur group occurred in the same order as those of the FeSO_4 group. In both cases maximum recovery came from the heavy MgO addition and the minimum from the heavy burnt-lime treatment. More than one-half of the total recovery from the sulfur control was obtained in the leachings of the first year, while still larger fractions came from the light treatments of CaO and MgO . The recovery from the 1000-pound-S-addition control during the first two years amounted to 75.1 per cent. The recoveries from the sulfur treatment and the two supplementary CaO and MgO treatments at the 2000-pound-plus rate, and the MgO treatment at the 32-ton rate during the same 2-year period, were 85.3 86.8 and 83.4 per cent, respectively.

Only about 10 per cent of the total recovery from the heavy burnt-lime treatment was found in the leachings of the first year. This small outgo of 88.6 pounds was a little more than twice the amount of sulfur precipitated in rain water during 1917, and nearly five times the outgo from the untreated control. It was followed by a material increase during the second year and a still greater increase to the maximum annual outgo during the third year. In this respect it was parallel with nitrate outgo. The average concentrations for those leachings carrying $\text{Ca}(\text{OH})_2$ during the first three years were 0.012719 N., 0.001564 N., and 0.000633 N., as obtained, respectively, from hydroxide occurrences in four of the five leachings of the first year, four of the five of the second year, and three of the six of the third year. The fact that after rainfall correction, the recovery of sulfur from the 1000-pound addition with 32 tons of CaO was only 676.9 pounds cannot be taken as proving the sulfification of only this amount. For, with the same rainfall correction, only 675.2 pounds were recovered from the 1000-pound sulfate sulfur addi-

tion with 32 tons of CaO. These two recoveries are remarkably close, and they might be construed as indicating the complete oxidation, though incomplete recovery, of the added flowers of sulfur.

Assuming complete leaching of rainfall sulfur and no sulfates derived from the supplies native to the soil, or basic treatment, over the 5-year period, the recoveries were 740.9 pounds from the control, 921.5 pounds from the light application of CaO, 977.5 pounds from the light application of MgO, and 676.9 pounds from the heavy burnt-lime addition. Applying the same assumptions to the maximum outgo of 1239.2 pounds from the 32-ton MgO addition, the recovery obtained was 1024.5 pounds or 24.5 pounds more than the addition. It is quite possible, however, if not probable, that some of the elementary sulfur applied to this group has not been converted into sulfates, and that the apparent respective recoveries are attributable in some measure to soil-derived sulfates.

By subtraction of the no treatment outgo from the 1239.2-pound outgo, an increased outgo of 63.4 pounds over the 1000-pound addition is accounted for. The lighter MgO treatment also gave sulfates in excess of the 1175.8-pound total represented by control outgo plus the 1000-pound addition. On this basis the light lime treatment failed of full recovery by 39.6 pounds, while 220.2 pounds and 284.2 pounds remained unrecovered in sulfur control and sulfur plus heavy lime treatment, respectively.

RELATION OF OUTGO TO PRECIPITATED SULFUR AND INITIAL SOIL CONTENT

No-sulfur additions. This relationship can be considered more directly in the case of no-sulfur additions in tanks 50 to 56, inclusive. Had there been no sulfur added from the atmosphere, the 5-year-period loss from the control would have amounted to 10.8 per cent of the initial sulfur content of the soil. This loss is accounted for by leachings ranging from the minimum of 18 pounds during the initial of subnormal rainfall to the maximum of 46.6 pounds as a result of a 54.75-inch precipitation during the third year. In the case of the leachings from the six alkali-earth additions, however, the losses ranging from 14.2 per cent to 17.1 per cent were the result, in every case, of a maximum during the first year, with progressive decrease to the minimum during the fifth year. These same six treatments gave sulfate losses ranging from 108.0 per cent to 129.7 per cent of the sulfur derived from rainfall. Only the control failed to leach as much sulfur as was derived from this source.

Additions. The sulfate recoveries from the added sulfate ranged from amounts equivalent to 54.6 per cent up to 81.1 per cent of the native sulfur content of the soil. The pyrite-addition group gave recoveries ranging from 25.4 per cent to 54.3 per cent of the amount originally contained by the soil. In the case of the elementary sulfur group, the range was from 54.7 per cent to 76.0 per cent. Each sulfur addition gave a recovery largely in excess of the sulfur brought down by rain, the smallest per cent excess of 192.7 came from

the heavy burnt lime and pyrite, while the largest 615.1 came from the heavy application of MgO with FeSO₄.

SUMMARY

Sulfate analyses of 614 collection from 22 lysimeters over a 5-year period are reported in a study of the loss of native stores of sulfureous materials and recoveries of sulfur derived from rainfall and 1000-lb.-per-acre additions of sulfur as FeSO₄, pyrite, and elementary sulfur, as such are influenced by various forms and amounts of calcic and magnesic materials.

The sulfate outgo from the no-treatment tank was less than that brought down by rainfall. Each of the treatments CaO, MgO, limestone, and dolomite at the 2000-lb., CaO-equivalent rate, and CaO and MgO, at the 3750-lb. rate, increased the outgo of sulfate sulfur to amounts somewhat in excess of those of the control and rainfall sulfur.

The unsupplemented FeSO₄ treatment, and also that with light supplements of both lime and magnesia and heavy supplement of magnesia, gave the largest annual recoveries during the first year. All three supplements also induced recoveries in excess of the recovery from the control, the totals coming in the order named. The heavy burnt lime treatment was initially very depressive to the outgo of the added sulfate radical. This effect was less marked after the first year, but its total recovery for the 5-year period was less than that of the sulfate control. The totals from the two light supplements and heavy magnesia were in excess of the sulfate addition. After deduction of rainfall sulfur, however, only the heavy MgO treatment gave a recovery equivalent to that of the addition.

The largest initial annual recovery and the largest 5-year total from the pyrite additions came from the acid-soil control. Both light and heavy supplements of lime and magnesia were depressive to sulfate leachings from the pyrite, the heavier applications having been decidedly more so than the lighter additions. In this respect the light additions differed from their activities upon FeSO₄ and sulfur. As in the FeSO₄ group, the heavy burnt lime was the most depressive of the four treatments.

Both CaO and MgO in light amounts and the heavy treatment of MgO accelerated the outgo of sulfates and increased the respective totals for the 5-year period when used as supplements to the powdered sulfur. The initial depressive influence of the heavy burnt-lime addition diminished after the first year, but its effect was still evidenced in the 5-year total, which was less than that of the control.

In agreement with previous work where no sulfur was added, increase in MgO additions caused increased sulfification of powdered sulfur and greater recoveries of added soluble sulfate. The lighter magnesia additions to both sulfur and ferrous sulfate caused smaller recoveries than the heavy MgO treatments and greater returns than those from additions of CaO. However,

the light CaO supplements to sulfur and FeSO₄ produced larger recoveries than were obtained from the respective sulfur and sulfate controls. The lesser recoveries from heavy CaO additions, to both sulfur and FeSO₄, were practically identical. It is not proved, therefore, that the minimum recovery from the sulfur group was due to the inhibitory effect of the heavy lime upon oxidation of the added sulfur.

Since the light application of MgO was more depressive than the corresponding CaO treatment to sulfate outgo from pyrite, while the heavy MgO was still more depressive, it is evident that the chemical or biochemical agencies responsible for the conversion of pyrite into sulfates differ from those responsible for the derivation of the same end-products from sulfur. For, both FeSO₄ and sulfur groups show that MgSO₄ would have been leached readily had it been present.

Disregarding the increment from rainfall, the recovery from both FeSO₄ and S controls during the first year was about one-half of that added, while that from pyrite was only about one-fifth of the addition. With the same inconsistency, the FeSO₄, sulfur, and pyrite controls had yielded 82, 83, and 68 per cent, respectively, of the sulfur additions after three years of leachings. In the order of light CaO, light MgO, and heavy MgO supplements, both sulfate and sulfur showed recoveries in excess of the 1000-pound additions at the end of the third year. With partial recovery from each pyrite addition, the same amendments induced recoveries in reverse order after three years.

After deducting the income from rainfall, only the recoveries of 1106.5 pounds and 1024.5 pounds induced by MgO from FeSO₄ and S, respectively, were in excess of the 1000-pound additions.

After deduction of the control sulfate outgo the recoveries from sulfate and sulfur additions with both MgO supplements were in excess of the added sulfur. On the same basis the other recoveries ranged between 237.9 pounds for pyrite and heavy burnt lime, to 988.6 pounds for FeSO₄ plus light lime treatment.

All 6 tanks treated with lime, or magnesia, without sulfur gave sulfate losses in excess of the amount precipitated during the 5-year period.

The continued depressive action of the heavy CaO treatment and the persistence of Ca(OH)₂ in the leachings were shown to be correlated. Conversely, carbonation of the excess of solid-phase Ca(OH)₂ and increase in outgo of sulfates from FeSO₄ and S additions were found to be parallel. The recovery of the initial depressive effect was much slower, however, in the case of pyrite.

Although the previously noted divergent effect of increasing amounts of CaO and MgO upon native sulfur stores was found to obtain also in the case additions of sulfur as FeSO₄ and "flowers," convergence was shown in the case of pyrite.

The results have certain practical significance. Economic and equivalent applications of burnt lime, magnesia, limestone, and dolomite were practi-

cally identical in their accelerative influences upon sulfification of native sulfureous materials. Oxidation of powdered sulfur was increased by small amounts of both lime and magnesia; but, undesirable losses may be caused by injudicious use in amounts which may be considered as within practical range. Pyrite may be considered as a source of sulfur, where less rapid generation is desired, particularly in an acid soil, since both lime and magnesia depress the amounts of water-soluble sulfates engendered. The use of excessive amounts of both CaO and MgO are inadvisable in connection with either sulfur or pyrite.

REFERENCES

- (1) ALLEN, E. T., AND JOHNSTON, J. 1910 The exact determination of sulphur in pyrite and marcasite. *In* Jour. Indus. and Engin. Chem., v. 2, no. 5, p. 196.
- (2) MACINTIRE, W. H., WILLIS, L. G. AND HOLDING, W. A. 1917 The divergent effects of lime and magnesia upon the conservation of soil sulfur. *In* Soil Sci., v. 4, no. 3, p. 231.
- (3) MACINTIRE, W. H., GRAY, F. J. AND SHAW, W. M. 1921 The non-biological oxidation of elementary sulfur in quartz media (preliminary report). *In* Jour. Indus. and Engin. Chem., v. 13, no. 4, p. 311.
- (4) MACINTIRE, W. H., GRAY, F. J. AND SHAW, W. M. 1921 The non-biological oxidation of elemental sulfur in quartz media.—A preliminary report. *In* Soil Sci., v. 11, no. 4, p. 249.
- (5) MACINTIRE, W. H. AND YOUNG J. B. 1923 Sulfur, calcium, magnesium and potassium content and reaction of rainfall at different points in Tennessee. *In* Soil Sci., v. 15, no. 3, p. 205–227.
- (6) MACINTIRE, W. H., SHAW, W. M. AND YOUNG, J. B. 1923 Influence of calcic and magnesian additions upon the outgo of sulfates from a loam soil, as measured by lysimeter leachings over an 8-year period. *In* Soil Sci., v. 16, no. 1, p. 1–40.
- (7) RUDOLFS, W. 1922 Oxidation of pyrites by microorganisms and their use for making mineral phosphates available. *In* Soil Sci., v. 14, no. 2, p. 135–147.
- (8) RUDOLFS, W. AND HELBRONNER, A. 1922 Oxidation of zinc sulfide by microorganisms. *In* Soil Sci., v. 14, no. 6, p. 459.
- (9) VAN BEMMELLEN, J. 1886 *Bijdragen tot de kennis van den Alluviaal bodem in Nederland.* Holkema and Warendorf, Amsterdam.

A PRELIMINARY STUDY OF THE EFFECTS OF SODIUM
CHLORIDE UPON ALFALFA GROWN IN SOLUTION
CULTURES¹

S. LOMANITZ

New Jersey Agricultural Experiment Stations

Received for publication June 27, 1923

Aside from the interest that attaches to the question of the effect of chlorides upon plants because of the fact that some potassic fertilizers come in the form of chlorides or contain varying amounts of sodium chloride, there is also the observation, made by investigators and farmers alike, that some plants are favored while others are harmed when grown in the presence of sodium chloride. Of recent work bearing upon this question, mention should be made of the investigations of Soderbaum (11), Tottingham (14), Krishnamurti Row (7), Trelease (16), Harlow (5), Schneidewind, *et al.* (9), and Guglielmetti (4). From their results it is obvious that different crops will have to be studied independently with respect to the influence exerted upon them by this compound.

The writer was led to take up the study of the effect of sodium chloride upon alfalfa, first, as a result of a previous investigation done jointly with Dr. G. S. Fraps (2), at the Texas Agricultural Experiment Station, in which it was found that alfalfa from various parts of the country differed greatly with respect to chlorine content, varying from about 0.2 per cent to over 1.0 per cent, expressed as sodium chloride. The possibility suggested itself that chlorine or sodium chloride may be of some benefit to this plant. Another reason was the desire to undertake a systematic study of the salt requirements of this plant in nutrient solutions, and it was thought advisable to obtain information with respect to the necessity of including a chloride, more especially sodium chloride, among the salts to be tested.

There is also of course the purely scientific interest in the still moot question as to whether chlorine is essential (as distinguished from advantageous) for the growth of at least some plants.

By way of a suggestive remark it may be pointed out that in view of the fact that in some local areas there exists a special alfalfa problem in the sense that alfalfa land may, for no apparent reason, cease to produce profitable crops, any data concerning the nutritional relations of this plant should be

¹ Paper No. 136 of the Journal Series, New Jersey Agricultural Experiment Stations, Department of Plant Physiology.

welcomed as possibly contributing towards an intelligent investigation of the causes underlying this trouble.

The preference for western over eastern alfalfa in the hay market may possibly be due to a difference in composition, manifesting itself in varying palatability, in which the chlorine content may well play a part.

This study must of necessity be of a preliminary character, since up to the present time comparatively little work, if any, has been done in the way of a systematic study of the salt requirements of alfalfa. There is no such mass of data relating to alfalfa as has already accumulated and is being added to continuously in the case of wheat, soy beans, buckwheat, and other plants. This is rather strange, considered from the standpoint of the economic importance of the alfalfa crop. The reason may be the fact that this plant, on account of its delicate initial growth, does not lend itself so easily to solution culture work as do plants with large seeds or those of a short growing period or of a sturdier habit of growth.

OUTLINE OF WORK

A commercial variety of alfalfa obtained from the seed testing laboratory of this station was germinated on blotting paper kept moist with a solution one-tenth the strength of the one used in the check solution culture. It was at first intended to obtain the average weight of single seeds and to use only those that approached very closely this average. But it was soon found that the seeds were very uniform in this respect, showing hardly any significant variation from the 2 mgm. average obtained on weighing a few lots of one hundred seeds each. A fine, even stand was secured after three days, at which time the seedlings were transferred to a germinating net, as described by Shive (10). On the third of January, 1923, when the seedlings reached a length of about 7 cm., they were put into the jars containing the culture solutions, according to the procedure adopted by Tottingham (13) and by Shive (10), using three plants to each jar. The cultures were run in duplicates and two series, A and B, were started at the same time. In series A the sodium chloride was introduced into the culture solution when the seedlings were first transferred to the jars. In series, B this addition was not made until the seedlings had grown in the check solution for five weeks. In every other respect the corresponding cultures of the two series were treated alike.

Eighteen jars, numbered 1 to 18, were used. The five different solutions to be described presently were numbered 1 to 5 corresponding to contents of sodium chloride equivalent to osmotic concentration values of 0.0, 0.1, 0.2, 0.3, and 0.4 atmospheres, respectively. Jars 1 and 2 served as checks and received solution 1; jars 3 to 10 made up series A; jars 11 to 18 made up series B.

Solution 1, used in the checks, was one of those used by Tottingham (13) and designated by him $T_1R_1C_5$. This solution was chosen for the check, since it was found by Jones and Shive (6) to give good growth with soy beans, the only leguminous plant so far which has been given a systematic study with respect to its salt requirement. The total concentration, in terms of osmotic pressure, was one atmosphere, made up of the partial concentrations in atmospheres of the four salts used in this solution as follows: potassium nitrate, 0.1; monopotassium phosphate, 0.1; calcium nitrate, 0.5; magnesium sulfate, 0.3 atmospheres. The corresponding volume-molecular concentrations are: 0.0020, 0.0021, 0.0073, and 0.007.

The other four solutions, designated 2, 3, 4, and 5 were made up by adding sodium chloride, in increments of 0.1 atmosphere, until the maximum of 0.4 atmospheres was reached, at the same time maintaining approximately the original total osmotic concentration by elim-

inating correspondingly equivalent amounts of one or more of the other salts. For the first 0.1 atmosphere of sodium chloride introduced, the 0.1 atmosphere of potassium nitrate of the original solution $T_1R_1C_6$ was eliminated, since the ingredients making up this salt are already present in some of the other salts (mono-potassium phosphate and calcium nitrate). In solutions 3 and 4, the further additions of sodium chloride replaced an equivalent and evenly distributed partial pressure of the other three salts. With solution 5, which contained 0.4 atmosphere of sodium chloride, the mono-potassium phosphate was restored to its original 0.1 atmosphere so as not to deprive the solution of two essential elements, the other two salts each being diminished by 0.1 atmosphere, thus bringing up the total concentration of this solution to 1.1 atmospheres.

The mere diminution in essential plant nutrients caused by eliminating part of the other salts should not be considered as in itself a factor of possibly grave consequences to plant growth, since previous studies with culture solutions by Trelease (15, p. 225) and others by Stiles (12) have brought out the fact that nutrient solutions within the range here used may vary considerably in either direction without showing any significant difference in their effect upon yield.

Sodium chloride of high purity was dried at 102°C. to constant weight, and a stock solution of 0.5 M concentration prepared. The formulae for the final dilutions were calculated and the culture solutions were finally prepared from the 0.5 M stock solutions. Iron in the form of a solution of ferrous sulfate was added at the rate of 0.1 mgm. of iron per liter of solution at the beginning; this amount was increased to 1 mgm. later.

The plants were grown in the greenhouse from January 3 to April 10, 1923, 98 days in all. During the last few weeks, half-gallon jars replaced the quart jars in which the plants were grown from the beginning. The solutions were renewed every three and one-half days.

Colorimetric determinations of the pH value of the discarded solutions, and occasionally of the original ones, were made according to the method of Gillespie (3), by means of the apparatus devised by Van Alstine (17), at various times during the growing period.

In the harvesting, drying, and weighing, the methods laid down in "A Plan for Co-operative Research" (8) were followed, omitting, however, the weighing of the green plants.

Determinations of total nitrogen and of chlorine were made separately of the tops and of the roots of the plants from each jar, following the analytical methods of the Association of Official Agricultural Chemists (1).

DISCUSSION OF RESULTS

Yield in dry weight

From table 1 and figure 1 it is seen that of the five solutions tested, solution 2, which is Tottingham's solution $T_1R_1C_6$ modified by replacing the 0.1 atmosphere of potassium nitrate with an equivalent amount of sodium chloride, gave the highest yield in tops, roots, and consequently of the whole plant. This relation holds good for series A where the sodium chloride was introduced into the culture solution from the beginning, as well as for series B where the sodium chloride was not supplied until the plants had grown in the check solutions for five weeks. The greatest increase over the check manifested itself in the roots, amounting to 147 and 169 for series A and B, respectively, as compared with the check taken as 100. The values for the whole plant for each of the two series A and B are in fairly close agreement being 15.064 gm. and 15.476 gm., respectively, for the actual weights; and 124.8 and 128.2, respectively, for the relative weights. All the other cul-

TABLE I
Effect of sodium chloride on yield, nitrogen and chlorine content of *alfalfa* grown in solution cultures (averages of duplicate cultures). Series A, sodium chloride used throughout the growth period, series B, sodium chloride introduced after plants had grown 5 weeks in the check solution

SOLUTION 1		SOLUTION 2		SOLUTION 3		SOLUTION 4		SOLUTION 5	
1 Löttingham's TIR/C ₄		0.1 atm. NaCl substituted for 0.1 atm. KNO ₃		0.2 atm. NaCl substituted for 0.1 atm. KNO ₃ and 0.033 atm. each of the remaining salts		0.3 atm. NaCl substituted for 0.1 atm. KNO ₃ and 0.066 atm. each of the remaining salts		0.4 atm. NaCl, 0.3 atm. substituted for 0.1 atm. each of KNO ₃ , Ca(NO ₃) ₂ and MgSO ₄ , and 0.1 atm. superimposed	
Check series	Series A	Series B		Series A	Series B	Series A	Series B	Series A	Series B
		Series A	Series B						
Dry weight, grams									
Tops.....	8.853	10.313	10.024	7.471	10.047	8.952	9.511	9.188	9.760
Roots.....	3.214	4.751	5.452	3.131	5.100	4.160	4.610	4.645	4.329
Whole plants.....	12.067	15.064	15.476	10.602	15.146	13.112	14.121	13.833	14.089
Relative weights	dry	Tops.....	100	116.5	113.2	84.4	113.5	101.1	107.4
		Roots.....	100	147.8	169.6	97.3	158.6	129.4	143.4
		Whole plants.....	100	124.8	128.2	87.8	125.5	108.6	117.0
Nitrogen content, per cent		Tops.....	4.02	3.89	3.63	3.49	3.49	3.39	3.55
		Roots.....	2.40	2.60	2.29	2.30	2.37	2.18	2.27
		Whole plants.....	3.58	3.40	3.16	3.20	3.12	3.01	3.12
Chlorine content, per cent		Tops.....	Trace	0.23	0.32	0.50	0.49	0.63	0.68
		Roots.....	Trace	0.15	0.12	0.16	0.18	0.20	0.30
		Whole plants.....	Trace	0.21	0.25	0.40	0.39	0.50	0.56

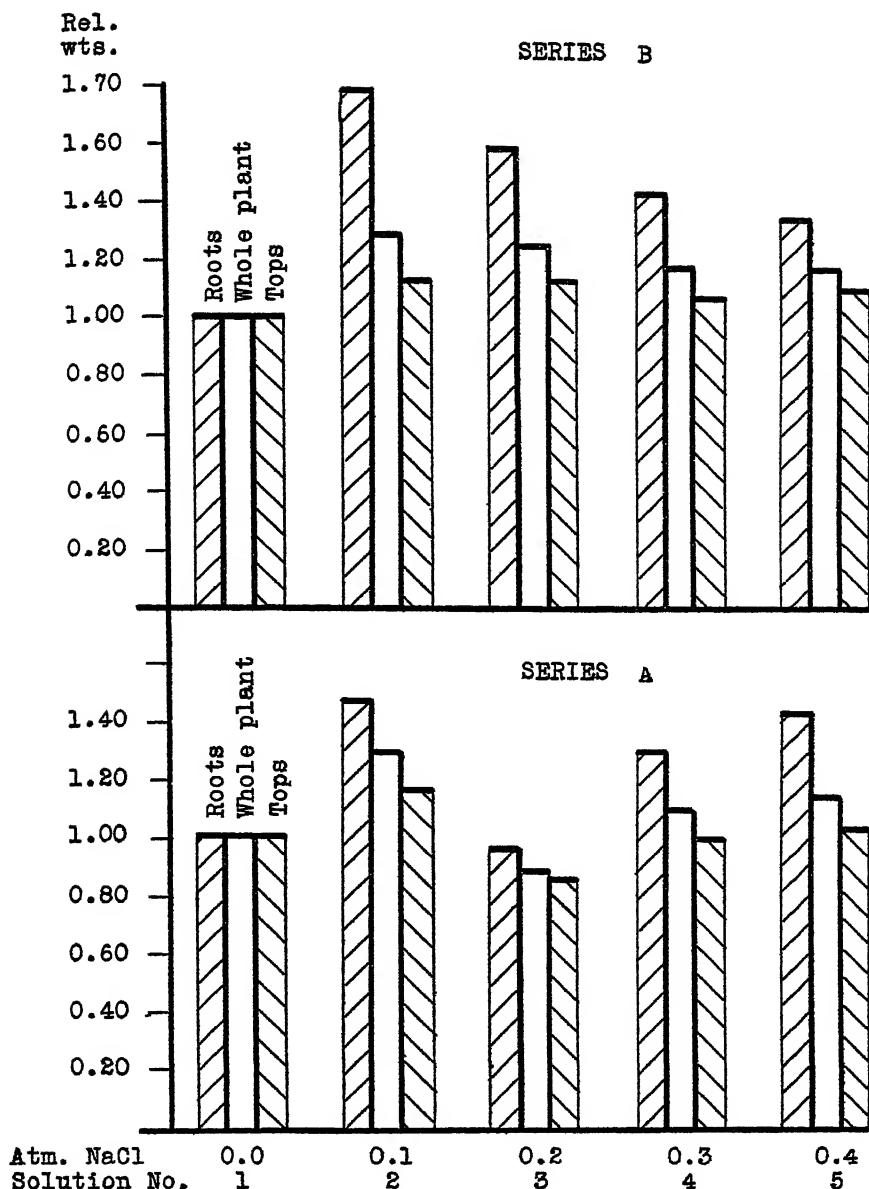


FIG. 1. GRAPHS SHOWING YIELDS OF TOPS, ROOTS, AND WHOLE PLANTS, RELATIVE TO CHECK (TOTTINGHAM'S SOLUTION T₁R₁C₈) TAKEN AS 100

Series A, sodium chloride supplied from the beginning. Series B, sodium chloride supplied only after plants had grown five weeks in check cultures.

tures containing sodium chloride, with the exception of one culture of solution 3 in series A, also gave considerable increases over the check. The decrease noted in the case of solution 3, series A, is obviously not related to the sodium chloride content of the culture, since the parallel culture of the same

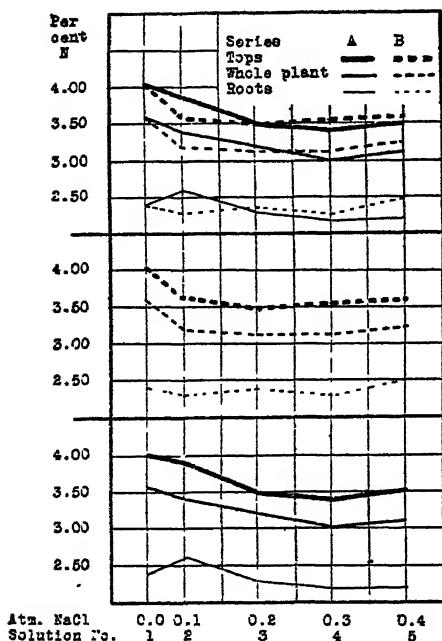


FIG. 2.

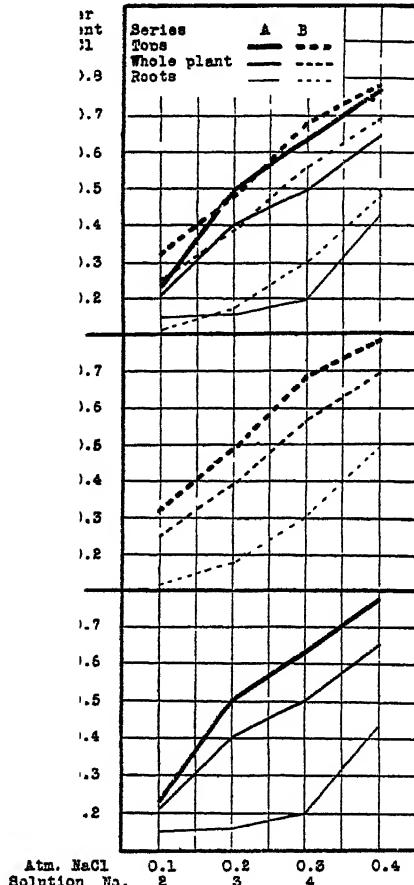


FIG. 3.

FIG. 2. GRAPHS SHOWING PERCENTAGE OF NITROGEN IN TOPS, ROOTS, AND WHOLE PLANTS

Series A, sodium chloride supplied from the beginning. Series B, sodium chloride supplied only after plants had grown five weeks in check cultures. First point on each graph represents value of check.

FIG. 3. GRAPHS SHOWING PERCENTAGE OF CHLORINE IN TOPS, ROOTS, AND WHOLE PLANTS

Series A, sodium chloride supplied from the beginning. Series B, sodium chloride supplied only after plants had grown five weeks in check cultures.

solution in series B gave an increase over the check, practically equalling the highest obtained, and solutions with higher concentrations of sodium chloride also gave increases in yield, as already pointed out.

It is therefore allowable to conclude, within the limits of this preliminary study, that the inclusion of a certain proportion of sodium chloride among the salts used for solution cultures will, in the case of alfalfa, affect the yield advantageously.

Nitrogen content

Data for the percentages of nitrogen in the tops, roots, and whole plant, on the dry basis, are also given in table 1. While some fluctuation will be noticed when only the tops of the plants grown in different cultures are compared, this is less noticeable when a similar comparison is applied to the roots, and there are only small differences in the nitrogen content of the whole plants. This is brought out in the graphs (fig. 2) representing the data for the percentage of nitrogen. The diminished supply of nitrogen caused by the elimination of the 0.1 atmosphere of potassium nitrate and the final reduction of calcium nitrate to four-fifths of the original amount did not appreciably affect the nitrogen content of the plant as a whole. It is evident also that of the total nitrogen in the plant, by far the greater part was contained in the tops.

Chlorine content

The amount of chlorine taken up by the plants in the different solutions increased uniformly with the amount supplied. This, as seen in table 1, applies to the tops as well as to the roots and to series A as well as to series B. The graphs representing the chlorine content are practically straight lines for the tops in both series, the two lines almost coinciding. The graphs representing the chlorine content of the roots also run close together for both series, lying rather flat in the concentrations of 0.1 to 0.3 atmosphere osmotic concentration of sodium chloride, and taking a steep pitch in the solution containing 0.4 atmosphere, but never reaching the high points attained by the tops. There is no appreciable difference in the chlorine content of either roots, tops, or whole plants of the parallel cultures of the two series.

Transpiration

While no quantitative transpiration measurements were made on the different solutions, the greater amount of water lost in solution 2, containing 0.1 atmosphere of sodium chloride and which produced the highest yield in both series, was too obvious to escape notice. This difference can be noted in a rough way by comparing the quantity of liquid left in jars 3 and 11 (Plate 1), which represent cultures of solution 2 in series A and B respectively, with any of the others.

Hydrogen-ion concentration

The figures obtained for the pH values at various intervals of growth confirm the observation made by a number of investigators, that culture

solutions of this type in contact with the roots of growing plants tend to approach the neutral point with the advance of the growing period. The initial pH value of the solutions was 4.7 except in the case of solution 4, with the smallest amount of mono-potassium phosphate, which showed a pH value of 5.0. The discarded solutions showed an increasing pH value as the growing period advanced, reaching a pH value of 6.0 in a $3\frac{1}{2}$ -day interval after the plants had been growing for three months. It is interesting to note that solution 4, which showed an initial pH value 0.3 higher than that of the other solutions, also showed a corresponding rise in the final pH value, which was 6.3 instead of the 6.0 of the other solutions.

SUMMARY AND CONCLUSIONS

1. Alfalfa was grown for 98 days in various culture solutions containing different amounts of sodium chloride, using as check the culture solution known as Tottingham's solution $T_1R_1C_5$.
2. The solutions containing sodium chloride gave higher yields than did the check.
3. The greatest increase was obtained with the solution in which 0.1 atmosphere osmotic concentration of sodium chloride was substituted for the 0.1 atmosphere of potassium nitrate of Tottingham's solution $T_1R_1C_5$.
4. The roots showed a greater relative increase than did the tops.
5. There was no appreciable difference in the nitrogen content of the whole plant, between the plants of the different cultures.
6. The chlorine content of the tops as well as of the roots increased uniformly with the increasing supply of that element, the tops, however, containing a larger percentage than the roots.
7. The greater part of both the nitrogen and the chlorine of the plant was contained in the tops.
8. The pH values of the discarded solutions approached gradually towards neutrality with the advancing growth of the plant.
9. Transpiration was highest in the case of the solution producing the largest yield.

ACKNOWLEDGEMENT

The ready assistance of Dr. John W. Shive of the Department of Plant Physiology, in the form of encouragement, suggestions as regards details of the work, and actual personal help at times, is hereby thankfully acknowledged.

REFERENCES

- (1) AMERICAN ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS 1921 Methods of Analysis, 2d ed., p. 7, 20. Amer. Assoc. Off. Agr. Chem., Washington, D. C.
- (2) FRAPS, G. S., AND LOMANITZ, S. 1920 The salt or sodium chloride content of feeds. Tex. Agr. Exp. Sta. Bul. 271.

- (3) GILLESPIE, J. L. 1920 Colorimetric determination of hydrogen-ion concentration without buffer mixtures, with especial reference to soils. *In Soil Sci.*, v. 9, p. 115-136.
- (4) GUGLIELMETTI, N. D. 1919 Action of water containing chlorides on cereals. *In Rev. Facult. Agron. y Vet., La Plata, ser. 2, v. 14, no. 1, p. 75-83., abs. in Exp. Sta. Rec.*, v. 45, p. 586.
- (5) HARLOW, L. C. 1920 The chlorin content of soils and fertilizer tests of salts. *Nova Scot. Secy. of Agr. Ann. Rpt. 1920, pt. 1, p. 117-122.*
- (6) JONES, L. H., AND SHIVE, JOHN W. 1923 Influence of ammonium sulfate on plant growth in nutrient solutions and its effect on hydrogen-ion concentration and iron availability. *In Ann. Bot., (in press).*
- (7) KRISHNAMURTI, ROW. 1919 Effect of salinity on growth and composition of sugar cane varieties. *In Agr. Jour. India, v. 14, no. 3, p. 476-493.*
- (8) NATIONAL RESEARCH COUNCIL 1919 A plan for coöperative research on the salt requirements of representative agricultural plants, 2d ed., Baltimore. 1919.
- (9) SCHNEIDERWIND, W., *et al.* 1920 Potash experiments. *In Landw. Jahrb., v. 55, p. 40-55.*
- (10) SHIVE, JOHN W. 1915 A study of physiological balance in nutrient media. *In Physiol. Res., v. 1, p. 327-397.*
- (11) SÖDERBAUM, H. G. 1918 New experiments in potash fertilization. *In Meddel. Centralanst. Forssk. Jordbruksomradet, no. 177, p. 1-14; abs. in Exp. Sta. Rec., v. 41, p. 723.*
- (12) STILES, W. 1919 On the relation between the concentration of the nutrient solution and the rate of growth of plants in water cultures. *In Ann. Bot., v. 29, p. 89-96.*
- (13) TOTTINGHAM, W. E. 1914 A quantitative chemical and physiological study of nutrient solutions for plant cultures. *In Physiol. Res., v. 1, p. 133-245.*
- (14) TOTTINGHAM, W. E. 1919 A preliminary study of the influence of chlorides on the growth of certain agricultural plants. *In Jour. Amer. Soc. Agron., v. 11, p. 1-32.*
- (15) TRELEASE, S. F. 1917 The relation of the concentration of the nutrient solution to the growth of young wheat plants in water cultures. *In Johns Hopkins Univ. Cir. 3, n. s., p. 225-228.*
- (16) TRELEASE, S. F. 1920 The relation of salt proportions and concentrations to the growth of young wheat plants in nutrient solutions containing a chloride. *In Philippine Jour. Sci., v. 17, p. 527-603.*
- (17) VAN ALSTINE, E. 1920 The determination of the hydrogen-ion concentration by the colorimetric method and an apparatus for rapid and accurate work. *In Soil Sci. v. 10, p. 467-478.*

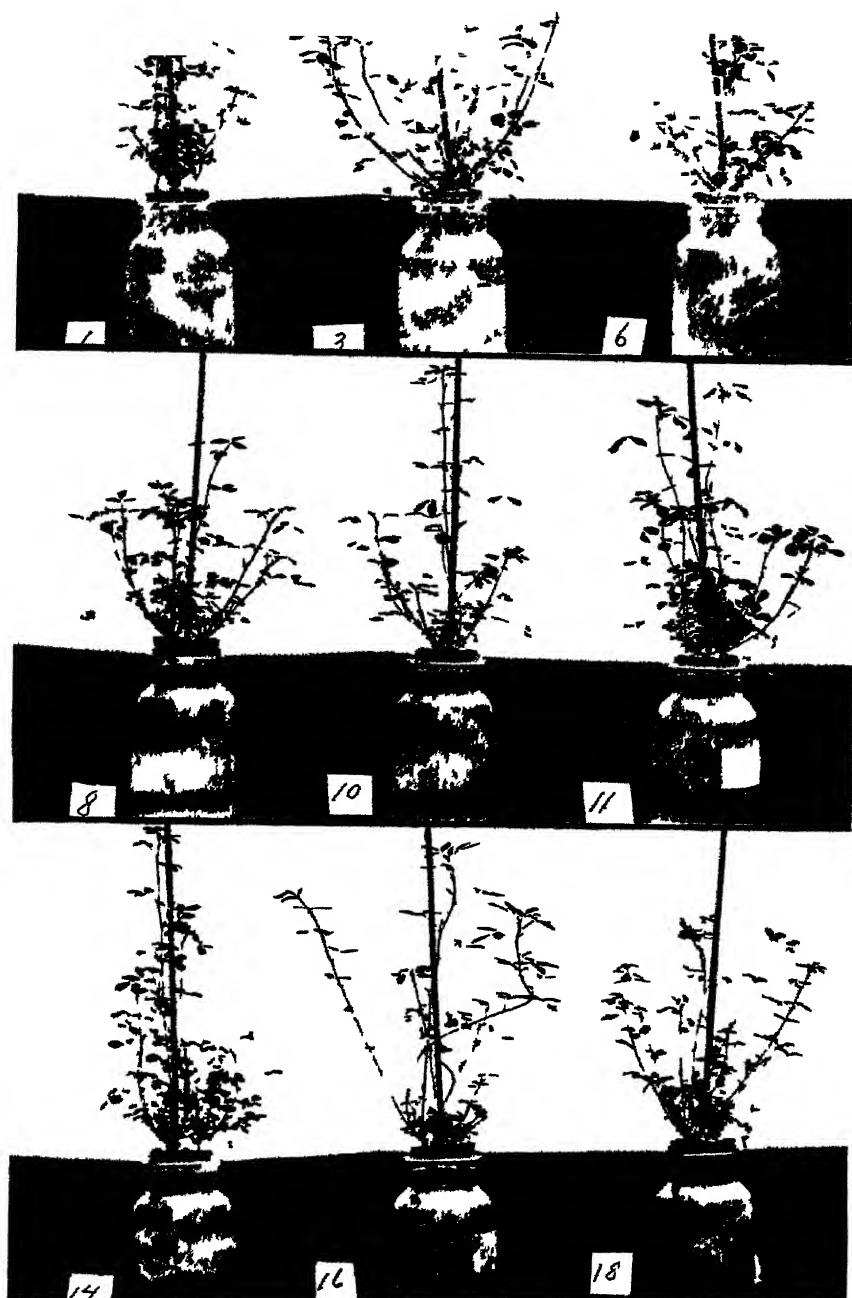
PLATE 1

ALFALFA NINE WEEKS OLD, GROWN IN SOLUTION CULTURES

- Series A. Jar 1, check.
Jar 3, 0.1 atm. sodium chloride.
Jar 6, 0.2 atm. sodium chloride.
Jar 8, 0.3 atm. sodium chloride.
Jar 10, 0.4 atm. sodium chloride.
- Series B. Jar 11, 0.1 atm. sodium chloride.
Jar 14, 0.2 atm. sodium chloride.
Jar 16, 0.3 atm. sodium chloride.
Jar 18, 0.4 atm. sodium chloride.

EFFECT OF NaCl ON ALFALFA IN SOLUTION CULTURES
S. LOVANITZ

PLATE 1



ACIDITY OF HIGHLY BASIC SOILS

W. T. McGEORGE

Experiment Station, Hawaiian Sugar Planters' Association

Received for publication May 28, 1923

Hawaiian soils while characteristically basic are with rare exceptions acid in reaction and usually show a high lime requirement by the Veitch method. On the other hand experiments and general observations have rarely indicated that sugar cane is benefited by liming these soils. As a whole the results indicate that sugar cane is indifferent to soil reaction or tolerates a certain kind of acidity. The question arises, what is the nature of this acidity?

Comparatively little work has been published showing the relation of lime requirement of soils as determined by the various methods to hydrogen-ion concentration in soils high in iron, aluminum and manganese oxides. In Hawaiian soils these oxides are often in excess of silica. Such a comparison has been recently made in this laboratory in order to obtain information relative to the nature of acidity in such types. To determine the merits of the different methods was not the purpose of this study.

SOILS USED

Fourteen soils were selected varying in pH values from 4.63 to 8.01. The composition of these soils as to the more important basic constituents and silica is given in table 1. The results are expressed on the air-dry basis in order to illustrate the variation of the moisture content of the soil in the air-dry state.

Soil 848 is a heavy black clay adobe soil high in water-soluble iron and aluminum from windward Oahu, irrigated land and low elevation.

Soil 849 is the subsoil to no. 848 and similar in texture and color.

Soil 367 is a yellow clay loam. The analysis of soil 399 is not given in this table because of its similarity to no. 367. Both are from the island of Kauai, upland soils from unirrigated fields.

Soil 186 is a sandy loam high in organic matter and combined water from Honokaa, island of Hawaii.

Soil 187 is the subsoil to no. 186 and similar in texture but lighter in color.

Soil 765 is a yellow silty loam from the Hilo-Hamakua district. Rainfall in this district is very heavy, land unirrigated, clay highly hydrated and high in organic matter.

Soils 621 and 408 are red clay loams from districts where rainfall is low. The former is from Lahaina, Maui, medium elevation and the latter from low elevation on Oahu, Ewa plantation.

Soil 409 is the subsoil to no. 408.

Soil 734 is a chocolate colored silt loam from a manganiferous area, an upland soil on the island of Oahu.

Soil 722 is a brown clay loam, island of Oahu, lowland irrigated land.

Soil 872 is the same type as no. 848 except taken from a section nearer the sea and high in coral.

Soil 3 is a sandy clay loam from Honolulu derived from volcanic ash and underlaid with it. While it is high in lime there is practically none present as carbonate.

These soils have been selected from sugar lands located on all the four major island, Oahu, Maui, Kauai and Hawaii and represent lowlands, uplands, humid and more or less arid districts.

TABLE 1
*Partial analyses of soils**

SOIL NUMBER	TiO ₂	Fe ₂ O ₃	Al ₂ O ₃	Mn ₂ O ₄	CaO	SiO ₂	LOSS ON IGNITION	
							H ₂ O	Organic matter, etc.
848	6.0	11.17	19.33	0.18	1.23	40.9	12.47	10.63
849	7.2	10.37	18.88	0.13	1.42	39.8	14.20	9.11
367	12.2	22.54	28.51	0.20	0.61	9.8	9.06	15.80
765	8.0	22.54	15.46	0.25	1.15	15.1	12.03	11.57
186	6.0	13.56	15.09	0.26	1.23	13.2	19.60	29.63
187	4.4	13.56	18.04	0.25	1.01	17.5	22.20	29.63
621	7.4	21.74	27.36	0.30	0.98	31.7	4.11	10.69
409	10.0	15.56	25.64	0.22	0.84	33.8	9.10	9.09
734	5.8	14.16	28.79	1.10	0.92	33.9	8.90	11.25
722	9.8	15.76	29.24	0.43	0.86	31.0	6.04	13.34
408	9.4	14.56	26.04	0.77	0.99	33.7	7.70	11.5
872	5.6	13.96	15.44	0.34	3.14	42.3	9.17	10.58
3	5.9	23.74	15.51	0.40	3.25	30.8	7.00	10.24

* Analyses by fusion with sodium carbonate.

METHODS USED FOR DETERMINING LIME REQUIREMENT

The lime requirement or acidity of a soil is usually attributed to such phenomena as the actual presence of mineral or organic acids, absorptive or adsorptive properties of colloidal material, free hydrogen ions or the presence of certain specific compounds which on hydrolysis or replacement increase the hydrogen-ion concentration of the soil solution.

Extensive reviews of the various methods are available (1) which makes such a review unnecessary here. Those used in this investigation include the treatment of the soil with the salts of strong acids and strong bases, for example the Hopkins method (2) which calls for the use of KNO₃ or KCl; weak acids and strong bases, for example the Jones method (3) using a solution of calcium acetate, the Loew (10) method using potassium acetate and the Carr (5) method using KSCN; weak acids and weak bases for example the Truog (12) method using zinc sulfide. Other methods include the Veitch (13) and the Hutchinson and MacLennan (9, p. 75) methods which utilize solutions of Ca(OH)₂ and CaH₂(CO), respectively, the Lyon and Bizzell method (4) in which Ba(OH)₂ is used in a somewhat similar manner, the Conner method (6) and that of Rice and Osugi (11) in which the hydrolysis of esters and sucrose respectively are used, Hollemann's method (9, p. 81) which measures the percentage

of lime soluble in water saturated with CO_2 , and Immendorf's method (9, p. 82) in which a back titration of 0.2 N H_2SO_4 in which the soil has been boiled is used.

A number of qualitative tests were also applied to these soils which include the litmus test, those of Veitch and Truog already described, the Comber method (7) which uses an alcoholic solution of KSCN and the Loew (10) method which uses a solution of KI in starch paste and as modified by Daikuhara using starch iodide paper instead of starch paste as a test for free iodine.

QUALITATIVE METHODS

The results obtained by the qualitative methods are given in table 2.

Of the above qualitative methods the litmus, Veitch and Comber appear to be best suited to local soil types as an indication of absence of adequate lime supply. The Loew and Truog methods appear to be of little value taking the pH values as a standard for comparison. The reaction involved in the two latter methods requires the presence of an acid which in the Loew and Loew-

TABLE 2
Qualitative tests for acidity

SOIL NUMBER	REACTION BY VARIOUS METHODS						pH VALUES
	Litmus	Veitch	Loew	Loew Dak.	Truog	Comber	
848	Acid	Colorless	Blue	Colorless	Positive	Dark red	4.63
849	Acid	Colorless	Blue	Colorless	Positive	Dark red	4.80
367	Acid	Colorless	Colorless	Colorless	Positive	Faint red	4.88
399	Acid	Colorless	Colorless	Colorless	Negative	Faint red	4.97
765	Acid	Colorless	Colorless	Colorless	Negative	Faint red	5.56
186	(?)	Colorless	Colorless	Colorless	Negative	Faint red	5.73
187	(?)	Colorless	Colorless	Colorless	Negative	Faint red	5.98
621	(?)	Colorless	Blue	Colorless	Negative	Faint red	5.98
409	(?)	Colorless	Colorless	Colorless	Negative	Faint red	6.32
734	(?)	Colorless	Colorless	Colorless	Negative	Colorless	6.66
722	Neutral	Colorless	Colorless	Colorless	Negative	Colorless	7.00
408	Neutral	Colorless	Colorless	Colorless	Negative	Colorless	7.08
872	Alkaline	Red	Colorless	Colorless	Negative	Colorless	7.67
3	Alkaline	Red	Colorless	Colorless	Negative	Colorless	8.01

Daikuhara methods sets free iodine from KI as indicated by the starch paste of starch iodide paper and which in in the Truog method liberates H_2S from ZnS as indicated by the lead acetate test paper. These methods apply only in those soils with pH values of 4.8 or less and indicate that these reactions are inhibited in our soil types or that in those soils of low hydrogen-ion concentration the small amounts of iodine or H_2S are absorbed and not set free on boiling. The Comber method showed some promise of yielding information relative to the nature of acidity and in view of this fact and the more advanced conceptions of soil acidity in which the salts of iron and aluminum play an important part more time was devoted to a study of this method. The reagent used in this test is an alcoholic solution of KSCN which will, in the presence of soluble iron, increase the concentration of $\text{Fe}(\text{SCN})_3$ in the liquid phase to

such an extent as to greatly increase the delicacy of the reaction. From the composition of Hawaiian soils one would ordinarily attribute acidity to be in a large part due to these elements.

According to Comber the red color increases in depth on standing. As thus applied to Hawaiian soils MnO_2 which is present in varying amounts in practically all types introduces a factor which within a certain pH range materially enhances the value of this method or viewed in another light may add to its value. In table 3 are noted the observations made with this test immediately after the soil had settled and at the close of 24- and 48-hour periods.

TABLE 3
Showing the factor of time in the Comber method

SOIL NUMBER	pH VALUES	COLOR REACTION AT CLOSE OF VARIOUS PERIODS OF TIME		
		15 min.	24 hr.	48 hr.
848	4.63	Dark red	Dark red	Dark red
849	4.80	Dark red	Dark red	Dark red
367	4.88	Light red	Light red	Light red
399	4.97	Red	Red	Red
765	5.56	Red	Red	Red
186	5.73	Light red	Light red	Light red
187	5.98	Light red	Light red	Light red
621	5.98	Light red	Blue	Blue
409	6.32	Light red	Blue	Blue
734	6.66	Colorless	Blue	Blue
722	7.00	Colorless	Blue	Blue
408	7.08	Colorless	Blue	Blue
872	7.67	Colorless	Colorless	Blue
3	8.01	Colorless	Colorless	Colorless

This blue color was found to be due to MnO_2 and it is apparent from table 3 that we may expect soils of pH less than 5.5 to show a permanent test for soluble iron. Within the range of pH 5.5-7.0, MnO_2 will change the red color to a greenish blue. This change in color is due directly to the MnO_2 and not to soluble manganese salts. For example, on adding MnO_2 to 848 there resulted a gradual fading to a blue while on adding manganese salts there was no change in color, the red color of undissociated $Fe(SCN)_3$ being permanent.

It was further suggested by Comber that if $FeCl_3$ be added to this reagent thus developing the red color before shaking with the soil, the iron present in the liquid phase will be displaced by lime in alkaline soils. As thus applied to the soils under investigation further peculiarities were met. The observations noted were as follows. In soils 848 to 187 there was no greater amount of color than where no $FeCl_3$ was added. Soils 621 to 408 all showed no greater amount of color and turned blue in 24 hours. While 872 and 3 remained colorless. The results clearly show the high absorptive capacity of the soil colloids and the influence of hydrogen-ion concentration on the color of the

$\text{Fe}(\text{SCN})_3$. The delicacy of the reaction in these soils is greatly increased by using an ether-alcohol reagent.

TABLE 4
Comparison of pH values with lime requirement in pounds CaCO_3 per acre

SOIL NUMBER	pH VALUES	LIME REQUIREMENT BY VARIOUS METHODS						
		Veitch	H-MacL	Lyon-Biz.	Hopkins	Loew	Jones	Carr
	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
848	4.63	11460	11080	11480	3570	9360	6840	7020
849	4.80	11460	13440	12820	6880	11580	8570	9000
367	4.88	6390	9070	8060	170	3630	4860	1200
399	4.97	6750	6720	7990	100	3510	3600	
765	5.56	15120	11500	12300	100	4410	6480	4290
186	5.73	22500	9820	13230	170	6480	6480	2200
187	5.98	24510	9570	11380	170	2490	5580	1000
621	5.98	2340	1510	250	85	1480	1260	
409	6.32	1350	2680	200	60	810	900	
734	6.66	1350	3520	120	40	1080	1260	
722	7.00	660	126	60	40	420	360	
408	7.08	1680	126	310	40	330	360	
872	7.67	660	-2680	Alk.	Alk.	270	Alk.	
3	8.01	660	-6630	Alk.	Alk.	210	Alk.	

TABLE 5
Comparison of pH values with lime requirement determinations

SOIL NUMBER	LIME REQUIREMENT BY VARIOUS METHODS			
	Rice Osugi	Conner	Immendorf	Hollemann
	gms. CuO per 2.5 gm. soil	cc. 0.5 N alkali per 10 gm. soil	cc. 0.2 N acid neutralized by 10 gm. soil	per cent CaO soluble in CO_2 -saturated water (1 part soil to 5 parts water)
848	0.0750	9.6	13.25	0.008
849	0.1160	4.4	13.40	0.007
367	0.0190	13.0	8.50	0.009
399	0.0130	10.0	7.75	0.013
765	0.0536	24.0	15.90	0.015
186	0.0254	10.0	20.25	0.017
187	0.0520	6.0	20.10	0.016
621	0.0150	8.0	10.00	0.023
409	0.0025	2.8	11.75	0.020
734	0.0050	10.0	14.90	0.023
722	0.0153	2.0	15.10	0.033
408	0.0136	2.8	13.00	0.027
872	0.0395	4.4	21.10	0.081
3	0.0230	2.0	24.10	0.131

QUANTITATIVE METHODS

A comparison of the quantitative methods of determining acidity or lime requirement with pH values is given in tables 4 and 5. Table 4 includes those

methods which express lime requirement as pounds of CaCO_3 per acre and table 5 includes those in which other terms are used.

Let us first consider the results obtained with the Veitch, Hutchinson-MacLennan and Lyon-Bizzell methods which, in a manner, involve similar principles. In the two former methods, amelioration of soil acidity is effected by methods closely resembling field practice, a solution of $\text{Ca}(\text{OH})_2$ in the one case and $\text{CaH}_2(\text{CO}_3)_2$ in the other. It is evident, however, that in addition to a neutralization of actual acidity and a replacement of soluble iron, manganese and aluminum the acidity will appear greater than it really is because of the physical absorption by the colloids. This extra lime, however, may be of benefit to the soil in other ways than neutralization of soil acidity.

In the results obtained by these three methods there is a general agreement in the soils with pH values of 4.6-5.5. Soil 186 and subsoil 187 show a wide variation. It is evident that this type of acidity is due to several acid constituents as shown by the different degrees of reaction with the different basic combinations. Absorption as a factor in this soil might be interpreted from the high content of water of hydration and the resulting colloidal properties usually associated with such types. Comparing soils 187 and 621 it will be noted that both show a pH of 5.98 while there is a difference of 10 tons lime requirement by the Veitch method, 4 tons by the Hutchinson-MacLennan method, and 5.5 tons by the Lyon-Bizzell method. These results indicate a high potential acidity in the former probably due to the presence of acid-reacting organic compounds and an acidity of greater intensity in the latter soil which has a lower organic content. The soils of lower hydrogen-ion concentration given in the table all show a greater degree of variation. In general it may be said that these methods neutralize all types of acidity and will usually agree closely enough for practical purposes on all our highly acid types where the ratio of lime absorbed by the colloids to that used in neutralizing acidity is low. But in those less important soils with pH values of 6-7 in which there is a higher ratio of absorbed lime to that neutralizing the soil acids, there is greater variation and less agreement, the Veitch method showing absorption even in the alkaline soils. Specific information relative to the nature of the acidity is wanting except that the Veitch method gives higher results (compared to the actual hydrogen-ion concentration on soils the acidity of which is due to organic matter) than where due to factors other than organic matter. In other words, the Veitch method has the advantage in the case of soils of high potential acidity where it is desired to estimate the lime needed to neutralize the soil, since in such types this factor is not indicated by the hydrogen-ion concentration.

In the Hopkins, Jones, and Loew methods we have the much discussed acidity by replacement or absorption. It is generally conceded that these methods indicate mineral acidity which is shown by the presence of aluminum, iron and manganese in the extracts of soils treated with solutions of the salts which are the basis of the above methods and supported by the fact that the

salts of these elements react acid through hydrolysis. Practically all soils show a higher acidity where acetates are used than with chlorides or nitrates and this is strikingly true of Hawaiian soils. Even in our most acid types it will be noted that the lime requirement as indicated by the Hopkins method is practically negligible. Both KCl and KNO_3 were used and the results obtained with both salts checked very closely. It is significant that the highest results were obtained on the soils of highest hydrogen-ion concentration and in which soluble iron and aluminum salts were present in large amounts, and that in these soils potassium acetate gave higher results than the calcium acetate.

The Conner method and Rice-Osugi method show a wide variation in the hydrolytic action of these soils as measured by the hydrolysis of sucrose and ethyl acetate. These compounds are hydrolysed or decomposed in the alkaline soils as well as the acid and there appears to be little relation between the hydrogen-ion concentration and hydrolysis indicating that this reaction is due in part to other factors than acidity.

The Immendorf method which acts as a measure of the soluble bases is of little or no value in these highly basic soils either as a measure of lime requirement or as indicating the nature of acidity. All the acid extracts of these soils were high in iron and aluminum except for soil 3.

On the other hand the Hollemann method which measures the solubility of lime in water saturated with carbon dioxide shows a very close relation to pH values. There is a gradual increase in the solubility of lime in this reagent with decrease in hydrogen-ion concentration. These results clearly indicate that the solubility of lime is definitely associated with the hydrogen-ion concentration of these highly basic soils both as a neutralizer of actual soil acidity and in the replacement of iron, aluminum and manganese in the soil solution because of their relative positions in the electromotive series. The results obtained show beyond a doubt that acidity in Hawaiian soils is largely a question or presence of absence of readily available calcium compounds.

Carr (5) has developed a quantitative method from that of Comber using the red color of $\text{Fe}(\text{SCN})_3$ as an indicator after determining the pH value at which this salt becomes colorless. As thus applied to Hawaiian soils some interesting results were obtained. In highly acid soils which give a positive test for iron the titration is to a greenish blue rather than a colorless solution. A pH value of 5.4 is the turning point and the change is rather indefinite. However in titrating from colorless or blue to red the change is even yet more indefinite and in the highly manganiferous soils considerable acid may be added without changing the pH value. For example, an acid-reacting soil containing 7 per cent MnO_2 , having a pH value of 5.9, on titrating with 0.1 N alcoholic H_2SO_4 still showed a pH value of 5.6 after adding 120 cc. and the red color of $\text{Fe}(\text{SCN})_3$ had not yet appeared. These observations are of considerable value in interpreting the rôle of manganese in the acidity of our manganiferous soils. Where appreciable amounts of manganese are present

as dioxide this compound will tend to stabilize the soil reaction and maintain a certain definite range of hydrogen-ion concentration.

DISCUSSION

In attempting an interpretation of this data as a whole, the results show that the acid soils of the humid districts will contain considerable acid-reacting organic matter of high potential acidity not indicated in the hydrogen-ion concentration. Such types will usually show a very high lime requirement but not necessarily a low pH value. Other factors may be absorption or adsorption, presence of silicic acid, complex acid-reacting silicates and hydrolyzable salts of aluminum, iron and manganese.

TABLE 6
Fe₂O₃ and Al₂O₃ in the salt extracts of acid soils

SOIL NUMBER	pH VALUES	per cent	
		IN KNO ₃ EXTRACT	IN KC ₂ H ₃ O ₂ EXTRACT
848	4.63	0.228	0.183
849	4.80	0.220	0.192
367	4.88	0.043	0.017
399	4.97	0.044	0.024
765	5.56	0.082	0.027
186	5.73	0.085	0.056
187	5.98	0.073	0.022
621	5.98	0.100	0.086
409	6.32	0.189	0.180
734	6.66	0.072	0.097
722	7.00	0.113	0.158
408	7.08	0.194	0.196
872	7.67	0.268	0.252
3	8.01	0.126	0.174

In ascertaining the rôle of these elements, their presence is usually sought in the salt solution extracts. Table 6 gives the percentage of iron and aluminum oxides in the potassium nitrate or Hopkins method extract and the potassium acetate method or Loew-extract of these soils.

It has usually been noted that (6) the aluminum content of the acetate extract is lower than that of the nitrate. This is explained theoretically by the difference in the hydrolytic products of the reactions involved, namely, aluminum acetate of which the products of hydrolysis are aluminum hydrate and free acetic acid and aluminum nitrate which is retained in solution as the acid salt. In the acid soils with reactions of pH 4.6-6.3, the iron and aluminum content is less in the acetate than in the nitrate extract. While in the soils with reactions of pH 6.6-8.0 this relation does not hold.

Judging from the color of the ammonia precipitate and qualitative tests, iron was present principally in the extracts of the most acid soils while scarcely more than a trace was found in the extracts of the soils with pH values of 6.0

to 8.0. It should be noted that the extracts of the alkaline soils contained just as much or possibly more iron and aluminum than those from the acid soils. The formation of acid salts is apparently inhibited by the association with higher soluble lime content.

This influence of easily soluble bases is apparently a very important factor. The solubility of silica and silicates is also of some importance. The ratio of iron, aluminum, calcium and silica was determined using 0.2 N nitric acid as a solvent and the results are given in table 7.

It will be noted that in all types easily soluble aluminum is far in excess of iron and highest in the highly organic soils. In general all four constituents show wide variations in the different soil types and there appears to be no

TABLE 7
Easily soluble bases and silica in 0.2 N nitric acid extract

SOIL NUMBER	SiO ₂ per cent	Fe ₂ O ₃ per cent	Al ₂ O ₃ per cent	CaO per cent	pH VALUES
848	0.120	0.032	0.468	0.435	4.63
849	0.137	0.026	0.052	0.396	4.80
367	0.012	0.005	0.313	0.051	4.88
399	0.012	0.100	0.182	0.108	4.97
765	0.097	0.022	1.518	0.145	5.56
186	0.252	0.043	3.920	0.423	5.73
187	0.386	0.032	3.830	0.141	5.98
621	0.067	0.008	0.175	0.176	5.98
409	0.105	0.007	0.138	0.202	6.32
734	0.270	0.004	0.537	0.278	6.66
722	0.116	0.006	0.233	0.253	7.00
408	0.141	0.009	0.174	0.269	7.08
872	0.287	0.031	0.602	1.045	7.67
3	0.493	0.011	1.585	1.185	8.01

relation between this ratio and acidity. Apparently the mineral acidity or hydrogen-ion concentration is not primarily entirely a function of the solubility of these elements but rather a function of other factors which limit the formation of acid or basic combinations.

Eliminating such abnormal types as soils 848 and 187 and considering only those in the series which are more typical of the average island soils, there is a tendency toward decreasing solubility of aluminum, less so the iron and an increase in soluble calcium with decrease in hydrogen-ion concentration. This ratio probably has an important bearing on the mineral acidity or acid reacting compounds of these elements.

EVIDENCE OF MINERAL ACIDITY OR PRESENCE OF ACID REACTING ORGANIC COMPOUNDS

As previously noted in the ammonia precipitates obtained on the nitrate and acetate extracts only traces of iron were found even in soils 848 and 849

both of which gave strong tests for soluble iron salts by the Comber method. This type of acidity is greatest in the heavy clay soils in which drainage is poor and aeration low and of which the above samples are typical. Iron then is not an important factor in the acidity of average island soils and its activity is confined to the most acid types and even in these evidently plays a secondary rôle to aluminum.

Manganese on the other hand is a factor only in those soils of low acidity. Of the manganeseiferous samples examined, the pH values were all 5.9 or higher. It was noted also that in an examination of the subsoils from these types that in all cases the subsoil was of a lower hydrogen-ion concentration than the top soil. Expressed in pH values the difference was 0.6 to 0.9 less acid. Judging from the relative positions of calcium and manganese in the electromotive series one would theoretically anticipate this to be true. The calcium apparently replaces the manganese in the soil solution which usually occurs on the soil grains as a coating, while the characteristically open texture of the manganeseiferous soils favors the leaching of lime into the subsoil.

Aluminum is present in easily soluble form in all the island types, highest in the humid districts and lowest in the arid. Apparently one of the principal rôles which lime plays in Hawaiian soils is in its relation to the acidity of aluminum salts which appear to be present in soluble form even in the alkaline types. This is best shown by the progressive increase in per cent of lime soluble in water saturated with CO₂ with increase in pH values and the further fact that aluminum appears to be present in equally available form in the acid and alkaline soils. In other words, the aluminum may be present either as an acid or neutral salt depending upon environment. It is significant that soil 186 represents a comparatively unproductive area, much less productive for example, than soil 848 which is much heavier and very poorly aerated. It has been found, in our island soils, that phosphate is much more available in the lowland sections than in the uplands. The principal inherent difference in the soils from such districts is the higher acidity and lower lime content of the uplands and a greater rainfall. A study of this phenomenon indicates that in the absence of lime in the more acid upland soils, phosphoric acid has combined with aluminum. The resulting compound has become hydrated and hence less available as there is no consistent difference in the total phosphate content of upland and lowland soils. The only variation is in the availability. It is believed that these facts lend some indication of the presence of acid mineral salts and that they are a factor in the acid reaction of island types.

The importance of silicates as a factor in this acidity appears to be at least closely related to that of aluminum. Silicates are present in Hawaiian soils in a comparatively soluble form as shown by its presence in the waters of the island streams and its solubility in the dilute and strong acid extracts of the soil. It will be noted in table 4 that the lime requirement as determined by potassium acetate is greatly in excess of that shown by extraction with a solution of potassium nitrate. In the case of aluminum silicate, the acidity

from potassium acetate is due entirely to acetic acid formed from the hydrolysis of aluminum acetate. There results a greater acidity than where acid salts are formed and relatively less aluminum in solution.

When anhydrides become hydrated they tend to assume acid or basic properties. This would apply to oxides of iron and aluminum as well as silicates and it is evident, therefore, that these compounds are more or less amphoteric depending upon environment. In our humid districts or those in which rainfall is heaviest a rapid leaching of lime has been noted. Where present as a double silicate of calcium and aluminum there may result a complex aluminum silicate containing no lime and of more acid tendencies. Soluble forms of lime have been found to be very low in the soils from these districts. The acid or neutral state of aluminum silicates will also depend upon the amount of water of hydration and ratio of silica to aluminum. Conner (6) found that ignition destroys the acid-reacting properties of clays as determined by the Hopkins method. Loss of water of combination therefore lowers the acidity of aluminum silicates. He found that those silicates of low water of combination were not acid and that those containing considerable water and silica were highly acid. Applying these theories to the island soils we find the soils from the districts of low rainfall to be low in acidity while the reverse is true of the soils from humid districts. Examples of the former are soils 621, 408, 409, 734, 722 while soils 765, 186, 187 will illustrate the latter. The higher organic content of the latter, however, must not be overlooked. The largest humid district under cane cultivation in Hawaii is the Hamakua coast section on the island of Hawaii. Available lime and potash are low in this section and water of combination or hydration high. The moisture content of the air dry soils is often as high as 25 per cent and the maximum water-holding capacity over 100 per cent. Such conditions actively favor the formation of acid aluminum silicates. There is a notable response to potash fertilization in this district indicating the absence of available forms of potash silicates. There is a progressive decrease in rainfall from the Hilo section of this coast to the Kohala district at the northern most extremity of the island. Accompanying this decrease in rainfall there is a decrease in maximum water-holding capacity, water of hydration and acidity of the soil. These observations tend to prove that the acidity of our humid districts is due in large part to alumino-silicic acids or acid silicates. In the more arid districts where cane is grown under irrigated conditions, rainfall being too low to support maximum growth, we find more lime present in soluble forms. In these districts there is decidedly less response to potash manuring. It may be of interest to state that the water of hydration is lower in the soils from these districts. We have under these conditions more active double silicates of potash, lime, soda or magnesia and aluminum which partially prevent the formation of alumino-silicic acids through neutralization.

SUMMARY

In this paper are reported the results obtained by the Hopkins, Jones, Loew, Carr, Truog, Veitch, Hutchinson-MacLennan, Lyon-Bizzell, Conner, Rice-Osugi, Hollermann, Immendorf and hydrogen electrode methods of determining soil acidity as applied to soils high in oxides of iron and aluminum.

While some comments have been offered regarding the merits of these methods on such soil types the main purpose has been to interpret from the data the nature of the acidity in our island types of soil.

In the humid districts acid-reacting organic matter is an important cause of soil acidity while in those sections of low rainfall this is true to a far less extent.

Mineral acidity is due in most part to aluminum salts and aluminum silicates, the latter predominating in the humid districts. Iron is a factor only in the very acid soils with reactions of pH 4-6 while manganese is a factor only in those with pH values of 5.5 to 7.0. Water of combination or hydration is also an important factor of soil acidity in all types of soil studied.

REFERENCES

- (1) AMES, J. W., AND SCHOLLENBERGER, C. J. 1916 Liming and lime requirement of soil. *Ohio Agr. Exp. Sta. Bul.* 306.
- (2) ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS 1908 Official and provisional methods of analysis. *U. S. Dept. Agr. Bur. Chem. Bul.* 107.
- (3) ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS 1915 Proceedings of the thirty-first annual convention held at Washington, D. C., November 16-18, 1914. *In Jour. Assoc. Off. Agr. Chem.* v. 1, p. 353-589, v. 2, p. 1-91.
- (4) BIZZELL, J. A., AND LYON, T. L. 1913 Estimation of the lime requirement of soil. *In Jour. Indus. and Engin. Chem.*, v. 5, p. 1011-1033.
- (5) CARR, R. H. 1921 Measuring soil toxicity, acidity and basicity. *In Jour. Indus. Engin. Chem.*, v. 13, pp. 931-933.
- (6) CONNER, S. D. 1916 Acid soils and the effect of acid phosphate and other fertilizers upon them. 1916 *In Jour. Indus. Engin. Chem.*, v. 8, p. 35-40.
- (7) COMBER, NORMAN M. 1920 A qualitative test for sour soils. *In Jour. Agr. Sci.*, v. 10, no. 4, p. 420-424.
- (8) COMBER, NORMAN M. 1922 A modified test for sour soils. *In Jour. Agr. Sci.*, v. 12, p. 370-371.
- (9) HUTCHINSON, H. B., AND MACLENNAN, K. 1915 Studies on the lime requirements of certain soils. *In Jour. Agr. Sci.*, v. 7, p. 75-105.
- (10) LOEW, OSCAR 1913 Studies on acid soils of Porto Rico. *P. R. Agr. Exp. Sta. Bul.* 13.
- (11) RICE, F. E., AND OSUGI, S. 1918 The inversion of cane sugar by soils and allied substances and the nature of soil acidity. *In Soil Sci.*, v. 5, p. 333-358.
- (12) TRUOG, E. 1915 A new test for soil acidity. *Univ. Wis. Agr. Exp. Sta. Bul.* 249.
- (13) VEITCH, F. P. 1904 Comparison of methods for the estimation of soil acidity. *Jour. Amer. Chem. Soc.*, v. 26, p. 637-662.

THE OCCURRENCE AND ACTION OF FUNGI IN SOILS¹

ERNEST V. ABBOTT

Iowa Agricultural Experiment Station

Received for publication June 26, 1923

Although soil fungi have been studied to some extent, our knowledge of the occurrence and functions of these organisms is still comparatively limited. In fact it is only recently that they have been looked upon as being of any importance in the soil. Many of the earlier workers considered them contaminations and believed their occurrence in the soil was accidental. Recent investigations have shown, however, that certain fungi may be more active than bacteria under some conditions, and that, although their functions as a whole are neither as varied nor as essential as those of many bacteria, they play an important rôle in soil fertility. Their wide distribution and large numbers, especially under conditions where bacterial growth is inhibited, indicate that they may take an active part in many soil processes.

That fungi exist in the soil in an active state is no longer open to question. Vegetative growth is often so abundant that the mycelium is plainly visible on the surface and within clumps of soil. This is especially true in the presence of large quantities of organic matter. But where the mycelium is not evident to the naked eye, its presence may be demonstrated with the method employed by Waksman (18). Furthermore, as Brown and Halversen (1) point out, "The presence of mold spores in a soil not only shows the previous occurrence of active forms, but what is more important, it shows the future growth of mycelial forms." Hence fungi undoubtedly have a potential influence, at least, on fertility.

Russell (15) has well stated the present situation regarding soil fungi when he says, "It is impossible on present knowledge to assess the importance of fungi in soil fertility. The decomposition of cellulose is undoubtedly important and justifies the old view that fungi are the humus formers of the soil. On the other hand the locking up of nitrogen compounds is a disadvantage, which, however, would be considerably counterbalanced if the substance of the mycelium were readily decomposable by bacteria on the death of the organism."

OBJECT

It is evident, then, that further work is needed to supply the true facts concerning soil fungi and to permit of the determination of their relation to

¹ The author wishes to express his appreciation to Dr. P. E. Brown and to Dr. Paul Emerson for outlining the problem and for many helpful suggestions during the course of the work, and to Dr. J. C. Gilman for his assistance in identifying the species.

soil problems. The purpose of the present work was to study certain activities of various fungi in soils, especially in relation to sulfur and phosphorus, which have received little attention heretofore.

Definite information regarding the fungous flora of the soil is very desirable. Until it is known with reasonable certainty what forms occur in the soil and just what reactions each organism will bring about, the actual importance of fungi in relation to soil problems cannot be definitely determined. While time has not permitted a complete determination of the fungous flora, members of the common soil genera have been isolated and studied in this work.

TAXONOMIC STUDIES

Five soils from the agronomy farm at the Iowa State College were used in the isolation work. The lime requirement of these soils varied from zero to 5 tons per acre as measured by the Truog method. The soil types represented and the crops growing on the soils were as follows:

SOIL TYPE	LIME REQUIREMENT	CROP
Webster clay loam.....	0	Clover
Webster silty clay loam.....	1 ton	Corn
Carrington loam.....	2 tons	Clover
Carrington loam.....	3 tons	Clover
Carrington loam.....	4-5 tons	Clover

Samples were taken in the usual way to depths of 3 to 4 inches, sterile instruments being used to prevent contamination. The soils were taken to the laboratory, dilutions made and plates poured immediately. The media used were modified albumen agar, Cook's No. 2 agar, Czapek's synthetic agar, and Waksman and Fred's (20) synthetic acid agar. Plates were poured in triplicate on each medium.

As soon as the colonies on the plates began to sporulate, transfers were made to agar slants. In many cases pure cultures were secured in this manner, but for most of the identification work single spore cultures were made according to the method described by Hagem (5). This method always gave satisfactory results after a little practise.

For identification, Thom's (17) sucrose potato agar was found most satisfactory as a general medium for all genera, since nearly all of the organisms studied developed and sporulated readily on this medium. The four media described by Thom (17) were used in identifying the members of the genus *Penicillium*, as well as some of the special differentiative media mentioned in his cultural data. Ordinary sterilized bread was found helpful in determining some of the *Mucors*.

As general guides in the identification, Rabenhorst (11) and Engler and Prantl (3) have been followed. Thom's key (17) was used in identifying the members of the genus *Penicillium*. Lendner (10) for the *Mucors*, Wehmeyer (21) for *Aspergillus*, while for other groups the works of Hagem (4), (5), (6), Jensen (7), and Oudemans and Koning (13) have been found very helpful.

The following species were isolated:

- | | |
|--|-----------------------------------|
| <i>Mucor glomerula</i> Lendner (Bainier) | <i>Aspergillus Koningi</i> Oud. |
| <i>Mucor geophilus</i> Oudemans | <i>Aspergillus glaucus</i> Link |
| <i>Zygorhynchus Vuilleminii</i> Namys. | <i>Aspergillus nidulans</i> Eidam |

<i>Rhizopus nigricans</i> Ehrenberg	<i>Aspergillus clavatus</i> Desmasières
<i>Penicillium luteum</i> Zukal.	<i>Aspergillus niger</i> van Tiegem
<i>Penicillium commune</i> Thom	<i>Aspergillus</i> sp.
<i>Penicillium expansum</i> Link	<i>Acrostalagmus albus</i> Preuss.
<i>Penicillium pinophilum</i> Hedgcock	<i>Acrostalagmus</i> sp.
<i>Penicillium funiculosum</i> Thom	<i>Cladosporium herbarum</i> Pers.
<i>Penicillium intricatum</i> Thom	<i>Chaetomella horrida</i> Oud.
<i>Penicillium rugulosum</i> Thom (?)	<i>Trichoderma Koningi</i> Oud.
<i>Penicillium decumbens</i> Thom (?)	<i>Verticillium</i> sp.
<i>Aspergillus fumigatus</i> Fres.	<i>Fusarium</i> sp.
<i>Aspergillus flavus</i> Link	<i>Monilia</i> sp.

PHYSIOLOGICAL STUDIES

The soil employed in the physiological studies was classified as the Carrington loam. In all the tests, 100-gm. portions of sieved, air-dry soil were thoroughly mixed with the organic or inorganic materials in question, placed in 250-cc. Erlenmeyer flasks, made up to the optimum moisture content, and sterilized in the autoclave for 15 minutes at 15 pounds pressure. On cooling, the flasks were inoculated with spore suspensions of pure cultures of the organisms.

For making the spore suspensions, a culture of the organism was grown on Thom's (17) sucrose potato agar for 5 to 7 days. Then 100 cc. of sterile, distilled water were added to the culture flasks, together with a little sterile sand to aid in breaking up the fruiting bodies, and the flasks agitated vigorously for several minutes until a good suspension of spores was secured. The flasks of sterilized soil were then inoculated with 1 cc. of this spore suspension by means of sterile pipettes and the inoculum mixed into the soil with a sterile spatula.

The soils were incubated at 26-28°C., the incubation periods varying with the different series. The moisture content was adjusted to the optimum every 10 days.

Ammonification

For determining the ammonifying powers of the organisms, cottonseed meal and dried blood were used as sources of organic matter, 2-gm. portions of each being supplied to the soil in duplicate flasks. Also, 22 cc. of distilled water, plus 2.5 cc. for each gram of organic matter were added to each flask. The flasks were sterilized, inoculated as noted above, incubated for 10 days, and the ammonia present determined by the aeration method (14). The results shown in table I are the averages of duplicate determinations. Where duplicates did not check well the experiment was repeated.

The results show that with few exceptions all the organisms were rather vigorous ammonifiers when either dried blood or cottonseed meal was used. With the single exception of *Acrostalagmus albus*, cottonseed meal proved a better source of nitrogen than dried blood for the fungi, the difference being very marked in some instances. *A. albus* produced a higher percentage of ammonia from dried blood than any other organism (3.57 per cent) and only slightly less from cottonseed meal (33.4 per cent). These results are in accord with those of Coleman (2), who found that cottonseed meal was more readily attacked by fungi than dried blood. McLean and Wilson (12), on the other

hand, obtained contrary results, more NH_3 being produced from dried blood, while Waksman (19) found a great variation in the ability of different species to attack the two materials, some preferring cottonseed meal and others dried blood. These variations were evident with members of the same genus.

With the exception of *Penicillium commune* and *P. pinophilum*, all of the organisms tested had a relatively high ammonifying power when tested with either dried blood or cottonseed meal. *Mucor glomerula* produced the highest percentage of ammonia from either source, liberating 65.4 per cent of the nitrogen in cottonseed meal, in the form of ammonia.

TABLE 1
Ammonification by fungi in 10 days

ORGANISM	DRIED BLOOD		COTTONSEED MEAL	
	Increase of $\text{NH}_3\text{-N}$ over check	Per cent ammonified	Increase of $\text{NH}_3\text{-N}$ over check	Per cent ammonified
<i>Asp. glaucus</i>	34.2	12.2	51.8	34.1
<i>Asp. fumigatus</i>	42.2	15.1	34.8	22.1
<i>Asp. Koningi</i>	47.7	23.2	64.9	43.3
<i>Asp. flavus</i>	31.9	10.6	26.2	18.4
<i>Asp. niger</i>	8.5	3.0	30.5	27.8
<i>Asp. sp.</i>	58.4	20.9	59.4	41.7
<i>Pen. expansum</i>	8.0	2.9	32.3	22.7
<i>Pen. commune</i>	-1.2	-0.4	6.0	4.2
<i>Pen. pinophilum</i>	1.3	0.5	14.1	9.9
<i>Pen. juniculosum</i>	55.4	19.8	39.2	27.5
<i>Pen. luteum</i>	59.0	20.0	39.8	28.0
<i>Mucor glomerula</i>	63.3	22.7	92.9	65.4
<i>Zygorhynchus Vuilleminii</i>	40.1	14.3	36.8	25.9
<i>Cladosporium herbarum</i>	10.7	3.8	30.9	21.7
<i>Acrostalagmus albus</i>	102.1	35.7	47.5	33.4
<i>Verticillium</i> sp.....	36.7	13.1	66.6	46.8
<i>Fusarium</i> sp.....	74.7	26.7	64.3	45.2
<i>Monilia</i> sp.....	94.4	34.9	54.9	38.6

In general, the species belonging to the imperfect genera were more vigorous ammonifiers than members of the genera *Aspergillus* and *Penicillium*. This is in accord with the results of previous workers (12), (19).

Phosphorus transformation

In this series, 10 gm. of sieved raw rock phosphate was thoroughly mixed with the air-dry soil, in flasks, 30 cc. distilled water were added, and the flasks were sterilized as noted above. The normal optimum moisture content for this soil was 22 per cent but the addition of the relatively large amount of rock phosphate made necessary a larger addition of water. At the end of the incubation period of 28 days, ammonium-citrate-soluble and water-soluble phosphorus were determined. The results are shown in table 2.

It is evident from the table that no water-soluble phosphorus was set free by the action of the fungi, since in every case the results, whether plus or minus, were so small that they fell within the experimental error. In view of the fact that similar results were obtained in other series the water-soluble determinations were discontinued.

Five organisms, *Aspergillus fumigatus*, *A. flavus*, *Penicillium funiculosum*, *P. luteum*, and *Cladosporium herbarum* appear to have had some action in setting free phosphorus as measured by the citrate-soluble method. This is especially true of *Cladosporium herbarum* and *Penicillium luteum* which liberated 24.9 mgm. and 22.6 mgm., respectively. It is possible that *Aspergillus niger* and *Penicillium pinophilum* which liberated 6.7 mgm. and 8.5

TABLE 2
Phosphorus transformation by fungi in 28 days

ORGANISM	CITRATE-SOLUBLE P		WATER-SOLUBLE P	
	In culture	Increase over check	In culture	Increase over check
	mgm.	mgm.	mgm.	mgm.
<i>Asp. glaucus</i>	27.1	4.9	0.22	-0.22
<i>Asp. fumigatus</i>	37.0	14.8	1.25	0.81
<i>Asp. flavus</i>	37.4	15.2	0.74	0.30
<i>Asp. Koningi</i>	32.3	5.1	2.06	1.62
<i>Asp. niger</i>	29.0	6.7	0.65	0.23
<i>Pen. expansum</i>	26.0	3.8	0.29	-0.15
<i>Pen. commune</i>	22.5	0.2	0.15	-0.29
<i>Pen. pinophilum</i>	30.7	8.5	0.15	-0.29
<i>Pen. funiculosum</i>	35.1	12.6	0.15	-0.29
<i>Pen. luteum</i>	46.1	22.6		
<i>Mucor glomerula</i>	26.9	3.4		
<i>Cladosporium herbarum</i>	47.1	24.9	1.10	0.66
<i>Acrostalagmus albus</i>	21.9	-1.6		
<i>Verticillium sp.</i>	23.4	-0.1		
<i>Fusarium sp.</i>	19.3	-6.2		
<i>Monilia sp.</i>	16.0	-7.5		

mgm., respectively, have had some effect on the phosphate rock, but not enough to be of any importance.

Only one other organism need be mentioned, *Monilia sp.* In this case there was a decrease of 7.5 mgm. below the check, which indicates that the organism utilized in its own metabolism the phosphorus which was set free, with a consequent locking up of phosphorus in the organic form. Further results would be necessary for definite conclusions. It is improbable that enough phosphorus would be locked up in the fungous bodies to have any permanent effect on plant growth, since on decomposition of the mycelium the phosphorus would again become available.

The phosphorus liberated may have been set free either by the action of the carbon dioxide or of the acids produced by the organisms. The ability

to produce rather large quantities of acid, especially oxalic and citric, is generally ascribed to fungi, and under laboratory conditions where relatively small quantities of soil are used, it is quite possible that sufficient acid would be formed to act upon the rock phosphate, rendering a portion of it soluble. From the field standpoint, however, it is probable that the action of carbon dioxide would be more important. Nearly all fungi attack organic matter, decomposing it quite readily, and it is reasonable to believe that the carbon dioxide produced in this decomposition process would have some effect on the insoluble phosphates in the soil. It has been suggested by Kopeloff (8) that fungi may be an important compensating factor in ammonia production in soil where conditions are unfavorable for bacterial growth. It is not improbable that under such conditions they may bear a similar relation to carbon dioxide production, and its resultant effects on inert materials in the soil.

Sulfur oxidation

In this experiment 2 gm. of flowers of sulfur were added to 100 gm. of soil in flasks, and treated as noted above. Sulfates were determined photometrically at the end of 10 and 20 days. The results are shown in table 3.

It is evident from the table that only one organism tested, *Penicillium luteum*, had any appreciable power of oxidizing sulfur. This organism liberated 17.1 mgm. of sulfate sulfur in 10 days and 20.3 mgm. in 20 days. The experiment was repeated with closely checking results. *Mucor glomerula*, which produced 6.9 mgm. in 20 days seemed to have had a slight action. All of the other results, whether plus or minus, were so small that they fall within the experimental error.

The amount of sulfate sulfur produced by *P. luteum* was one per cent of the application. Inasmuch as this organism has been isolated repeatedly and is one of the most common soil forms, it seems reasonable to conclude that it may be of importance in oxidizing sulfur in the field. It would be interesting to compare this organism with the sulfur-oxidizing bacteria. Where the latter are present in the soil it is probable, however, that their action would overshadow that of the fungus.

Seven strains of *P. luteum* were isolated, all very similar morphologically but quite different physiologically. On sucrose potato agar the colonies ranged in color from pure white in one strain to a brilliant red in another, while the other strains showed various intermediate gradations of color. The reverse of the colonies was also quite variable; some produced a pigment which diffused through the medium while others did not. The morphology of the organisms, however, was so nearly identical that it seems inadvisable to split the group into species, but to retain all of the strains in the "*Penicillium luteum* group." Detailed cultural data are not presented here as the group is being studied further. The strains so far tested were about equal in sulfur-oxidizing power.

TABLE 3

Sulfur oxidation by fungi in 10 and 20 days

ORGANISM	AFTER 10 DAYS' INCUBATION		AFTER 20 DAYS' INCUBATION	
	SO ₄ -S in culture	Increase over check	SO ₄ -S in culture	Increase over check
	mgm. of S	mgm.	mgm. of S	mgm.
<i>Asp. glaucus</i>	5.4	-5.0	6.4	0.1
<i>Asp. fumigatus</i>	9.5	-0.9	5.2	1.1
<i>Asp. Koningi</i>	12.0	1.6	7.0	0.7
<i>Asp. flavus</i>	9.1	-1.3	6.6	0.3
<i>Asp. niger</i>	6.2	-4.2	7.3	1.0
<i>Asp. sp.</i>	8.2	-2.2	6.1	-0.2
<i>Pen. expansum</i>	15.2	4.8	5.9	-0.4
<i>Pen. commune</i>	14.6	4.2	8.9	2.3
<i>Pen. pinophilum</i>	6.0	-4.4	5.9	-0.4
<i>Pen. funiculosum</i>	6.0	-4.4	10.9	4.3
<i>Pen. luteum</i>	27.5	17.1	26.6	20.3
<i>Cladosporium herbarum</i>	6.8	-3.6	5.8	-0.5
<i>Acrostalagmus albus</i>	5.8	-4.6	8.7	2.1
<i>Verticillium</i> sp.....	6.4	-4.0	5.0	-1.3
<i>Fusarium</i> sp.....	6.5	-3.9	8.4	2.1
<i>Monilia</i> sp.....	7.8	-2.6	10.0	3.7
<i>Mucor glomerula</i>	14.7	4.3	13.2	6.9

TABLE 4

Transformation of phosphorus by fungi in compositis of soil, raw rock phosphate and sulfur

ORGANISM	INCREASE OF CITRATE-SOLUBLE P OVER CHECK			INCREASE OF WATER-SOLUBLE P OVER CHECK	
	After 15 days	After 30 days	After 45 days	After 15 days	After 45 days
	mgm.	mgm.	mgm.	mgm.	mgm.
<i>Asp. glaucus</i>	-2.4	6.5	-4.8	0.1	-0.7
<i>Asp. fumigatus</i>	-11.6	-1.6	-1.1	0.2	-0.3
<i>Asp. flavus</i>	-6.6	3.7	-2.9	-0.1	-0.7
<i>Asp. Koningi</i>	-0.1	13.5	17.0	-0.1	-0.7
<i>Asp. niger</i>	-4.9	21.8	-2.0	0.1	-0.4
<i>Pen. expansum</i>	-7.6	3.9	-3.0	-0.3	-0.4
<i>Pen. commune</i>	-3.7	-1.2	-7.9	0.1	-0.0
<i>Pen. pinophilum</i>	-1.4	10.3	-10.8	0.0	-1.0
<i>Pen. funiculosum</i>	-1.2	7.5	10.5	0.2	-1.0
<i>Pen. luteum</i>	-3.4	11.2	3.3		
<i>Mucor glomerula</i>	-9.3	6.8	10.7		
<i>Verticillium</i> sp.....	-1.5	2.0	0.5		
<i>Fusarium</i> sp.....	-2.2	1.8	3.1		
<i>Monilia</i> sp.....	-6.4	19.3	-0.5		
<i>Cladosporium herbarum</i>	-4.0	4.2	-8.5		

Composts of raw rock phosphate and sulfur

In this experiment 10 gm. of raw rock phosphate and 2 gm. of sulfur were mixed with the soil. Citrate-soluble and water-soluble phosphorus were determined at the end of 15, 30, and 45 days. The results are shown in table 4.

Only three organisms, *Aspergillus Koningi*, *Penicillium funiculosum*, and *Mucor glomerula* showed consistent gains in the amounts of citrate-soluble phosphorus liberated. In each case the amount of soluble phosphorus increased at the end of the successive incubation periods, and the quantities were large enough to indicate some action by the organisms, being 17 mgm. with *A. Koningi*, 10.5 mgm. with *P. funiculosum*, and 10.7 mgm. with *M. glomerula*.

Comparing these results with those on phosphorus transformation where no sulfur was present, it will be noted that neither *Aspergillus Koningi* nor *Mucor glomerula* liberated a measurable quantity of soluble phosphorus in that series. This indicates that the sulfur added in this experiment had a stimulating effect on the ability of the organisms to attack the rock phosphate.

Since none of these three organisms has any measurable sulfur-oxidizing power and consequently would produce little or no sulfuric acid in the soil it is probable that the sulfur caused a stimulation of carbon dioxide production by the fungi, and that this carbon dioxide made more of the phosphorus soluble. The gradual accumulation of soluble phosphorus may be explained either by the fact that the organisms produced relatively large quantities of it or their phosphorus requirements were small.

With very few exceptions the remaining organisms tested showed a decrease under the check at the end of 15 days, a relatively large increase at the end of 30 days, and a decided decrease at the end of 45 days. It will be noted that *Aspergillus niger* and *Monilia sp.* showed appreciable gains in 30 days, while in 45 days they again fell below the check. A possible explanation of these results would be that the soluble phosphorus produced during the first 15 days was utilized by the growing organisms; then, during the next period, as the first "generation" died, the phosphorus was changed to a soluble state through autolysis of the fungous bodies. This period of quiescence was followed by the development of the second "generation" of fungi as the spores germinated, with the consequent utilization of the available phosphorus and a decrease in citrate soluble phosphorus.

As in the previous experiment, the results of the water-soluble determinations were such that no conclusions could be drawn from them.

DISCUSSION

The results as a whole indicate that fungi have a greater influence on the organic materials in the soil than on the inorganic. With the exception of two species all of the organisms tested were comparatively vigorous in their

action on the organic matter added to the soil, while few exhibited the power of attacking phosphorus and sulfur, and changing to a form available to plants. Many investigators, (5), (9), (16), (19), have shown that fungi are capable of decomposing complex organic materials in the soil, even attacking the complex, inert celluloses and breaking them down to a point where the decomposition may be completed by bacteria.

Undoubtedly fungi are of very great importance in soil as ammonifiers, probably being equal to bacteria in this respect, and available evidence indicates that their principal function in the soil is the decomposition of organic matter. Their effect on the mineral constituents appears to be more limited. Eight organisms showed the power of rendering a portion of the phosphorus in raw rock phosphate soluble, while only one was capable of oxidizing elemental sulfur. It cannot be stated, however, that fungi are of no importance in making such materials available under field conditions, because most of the common soil forms are active decomposers of organic matter, and they occur in such numbers that sufficient carbon dioxide would probably accumulate from the decomposition processes to act upon the complex mineral compounds. They would be especially important where conditions are such that bacterial growth is depressed.

Another fact which must be kept in mind is that in these experiments only pure cultures of fungi were used. It is the usual experience in microbiological work that mixed cultures, which more nearly represent natural conditions, give higher results than pure cultures, and it is quite probable that such would be the case here.

SUMMARY

1. In these experiments 28 species of fungi, representing 12 genera, were isolated from 5 soils which varied in lime requirement from zero to 5 tons per acre. The organisms isolated include the common soil genera, but represented a small proportion of the total soil flora.

2. Waksman and Fred's synthetic acid medium proved the most satisfactory for isolating fungi, since bacterial development is depressed on this medium.

3. With two exceptions, the organisms tested were rather vigorous ammonifiers. The members of the imperfect genera exhibited the greatest ammonifying ability while members of the genus *Penicillium* were the weakest.

4. All of the species tested ammonified cottonseed meal more readily than dried blood, with the single exception of *Acrostalagmus albus*.

5. Five species, *Aspergillus fumigatus*, *A. flavus*, *Penicillium funiculosum*, *P. luteum*, and *Cladosporium herbarum* were shown to have the ability of liberating soluble phosphorus from raw rock phosphate, as measured by the ammonium citrate method.

6. *Penicillium luteum* was the only organism tested which had the power of oxidizing free sulfur to the sulfate form. Seven strains of this organism were isolated, and all showed about the same sulfur-oxidizing power.

7. With composts of sulfur and raw rock phosphate, only three organisms, *Aspergillus Koningi*, *Penicillium funiculosum*, and *Mucor glomerula* showed consistent gains in the amount of citrate soluble phosphorus liberated through successive incubation periods of 15 days. With few exceptions the remaining species showed a decrease under the check in 15 days, an increase in 30 days, followed by a marked decrease in 45 days. It is probable that these variations correspond with the development of successive generations of the organisms.

REFERENCES

- (1) BROWN, P. E., AND HALVERSEN, W. V. 1919 Effect of seasonal conditions and soil treatment on bacteria and molds in soil. *Iowa Agr. Exp. Sta. Res. Bul.* 56.
- (2) COLEMAN, D. A. 1916 Environmental factors influencing the activity of soil fungi. *In Soil Sci.*, v. 2, p. 1-65.
- (3) ENGLE, A., AND PRANTL, K. 1897 Die Natuerlichen Pflanzenfamilien. Engelmann, Leipzig.
- (4) HAGEM, O. 1907 Untersuchungen ueber Norwegische Mucorineen I. *In Vidensk. Selsk., I Math. Naturw. Klasse*, v. 7, p. 1-50.
- (5) HAGEM, O. 1910 Untersuchungen ueber Norwegische Mucorineen II. *In Vidensk. Selsk., I. Math. Naturw. Klasse*, v. 10, p. 1-52.
- (6) HAGEM, O. 1910 Neue Untersuchungen ueber Norwegische Mucorineen. *In Ann. Mycol.*, v. 8, p. 265-286.
- (7) JENSEN, C. N. 1912 Fungous flora of the soil. New York (Cornell) *Agr. Exp. Sta. Bul.* 315.
- (8) KOPELOFF, N. 1916 Effect of soil reaction on ammonification by certain soil fungi. *In Soil Sci.*, v. 1, p. 381-403.
- (9) KOSOWICZ, A. 1912 Einfuehring in die Agriculturmykologie, v. 1, Borntraeger, Berlin.
- (10) LENDNER-HARSHBERGER 1917 Mycology and Plant Pathology, p. 697. Blakiston's Son & Co., Philadelphia.
- (11) LINDAU, G. 1910 Fungi Imperfecti, v. 1, part 8 of Kryptogamen-Flora von Deutschland, Oesterreich, und Oesterschweiz by L. Rabenhorst. E. Kummer, Leipzig.
- (12) MCLEAN, H. C., AND WILSON, G. W. Ammonification studies with soil fungi. *N. J. Agr. Exp. Sta. Bul.* 270.
- (13) OUDEMANS, C. A., OUDEMANS, J. A., AND KONING, C. J. 1902 Prodrome d'une flore mycologique obtenue par la culture sur gelatine preparée de la terre humeuse du Spanderswoud pres Bussum. *In Arch. Neerl. Sci. Nat.*, ser. 2, v. 7, p 286-298.
- (14) POTTER, R. S., AND SNYDER, R. S. 1914 The determination of ammonia in soils. *In Iowa Agr. Exp. Sta. Res. Bul.* 17.
- (15) RUSSELL, E. J. 1921 Soil conditions and plant growth, p. 259. London.
- (16) SCALES, F. M. 1915 Some filamentous fungi tested for their cellulose destroying power. *In Bot. Gaz.*, v. 60, p. 149-153.
- (17) THOM, C. 1910 Cultural studies of species of penicillium. *In U. S. Dept. Agr. Bur. of An. Indus. Bul.* 118.
- (18) WAKSMAN, S. A. 1916 Do fungi live and produce mycelium in the soil? *In Science n. s.*, v. 44, p. 320-322.
- (19) WAKSMAN, S. A. 1916 Soil fungi and their activities. *In Soil Sci.*, v. 2, p. 103-156.
- (20) WAKSMAN, S. A., AND FRED, E. B. 1922 A tentative outline of the plate method for determining the number of microorganisms in the soil. *In Soil Sci.*, v. 14, p. 27-28.
- (21) WEHMER, C. 1901 Die Pilzgattung Aspergillus in morphologischer, physiologischer und systematischer Beziehung unter die besonderen Berücksichtigung der mitteleuropaischen species. *In Mem. Soc. Physiol. Historie de Geneva*, v. 38, p. 1-57.

A 5-YEAR LYSIMETER STUDY OF THE SUPPOSED LIBERATION OF SOIL POTASSIUM BY CALCIC AND MAGNESIC ADDITIONS

W. H. MACINTIRE, W. M. SHAW AND J. B. YOUNG

University of Tennessee Agricultural Experiment Station

Received for publication May 21, 1923

INTRODUCTORY

It is widely believed that burnt lime and limestone effect a liberation of potassium from the potassic components, native to the soil. As a practical application of this belief, many users of agricultural lime have assumed that the potash requirements of crops would be cared for by the supposed replacement. This assumption has been based upon the fact that solutions of neutral salts of calcium and magnesium will effect basic exchange when soil and solution are agitated or when such solutions are percolated through a mass of soil. The development of this point of view may be traced by reference to bibliographies by MacIntire (6) and by Tressler (10). However, the imposed conditions under which the active mass of the alkalis and alkali-earths may effect basic exchange are different from those which prevail in the field. There the soil is bathed not alone by neutral salts, but also by the bicarbonates of calcium and magnesium derived directly from the excess of additions, or through hydrolysis of the silicates formed where all of the larger part of the additions are absorbed by the soil.

Experimental data on the problem are meager. In 1910, Wheeler (11) reported experiments begun in 1894, wherein lime was used alone and in conjunction with sodium chloride and with potassium chloride, with results which lead to the conclusion: "The results show that liming was of no great value on the Kingston soil, as a liberator of potash" Between May 13 and September 30, 1911, Brown and MacIntire (1) subjected freshly sampled moist borings from the burnt lime plat of tier II of the Pennsylvania Station to 17 aqueous extractions. They found an average concentration of potassium less than that dissolved from the control, which indicated that after a long period of liming the native potash was either decreased in quantity or depressed in solubility. MacIntire (5) later analyzed composites of all burnt lime and limestone plats for residual potash after 30 years of cumulative liming. The results obtained by the J. Lawrence Smith method led to the statement that: "A decrease in potash was noted in each case of lime treatment, but there was no correlation between residual lime and residual potash." These analyses were made upon composite samples from four plats of $\frac{1}{8}$ acre each. The variation in soil type and topography over the experimental area and the inherent

error of sampling such large plats militate against absolute dependability upon the findings reported.

Lipman (2) questioned the liberation of potassium by CaCO_3 in soils as a result of his extraction studies with calcium carbonate and calcium sulfate. Lyon and Bizzell (3) found no increase in the potassium content of leachings from their 4-foot tanks containing Dunkirk soil where a 3,000-pound addition of burnt lime was made. But, since the same observation was noted where potassium sulfate was added, it appeared that the vitiating influence of the subsoil would have masked any inter-change which might have taken place. The effect of a 3,000-pound addition of burnt lime to the Volusia soil appeared to be actually depressive upon the outgo of potassium salts through the 4-foot depth. As stated by these investigators (4), "There is nothing in this experiment to indicate that the application of lime caused the liberation of potassium. The same was true of the experiment with the Dunkirk soil. It may be remarked, however, that if the application of lime did liberate any potassium from the surface soil, it may have been absorbed by the lower layers of soil and thus have been removed from the drainage water."

MacIntire (6) reported results of a 5-year lysimeter study with shallow tanks containing only surface soil and deep tanks containing both soil and subsoil, seven different calcic and magnesic materials having been added to both series. The treatments ranged from 8 to 100 tons of the several materials on constant CaO-equivalent basis. It was found that lime and magnesia additions not only failed to liberate potassium to the leachings, but that an actual depression in potassium outgo resulted. It was recognized that liberation and reabsorption was possible, but evidence was advanced to minimize the validity of such an assumption. It was concluded that depressive influences of both lime and magnesia were due to the fact that H_2CO_3 was a more active solvent than either $\text{CaH}_2(\text{CO}_3)_2$, or $\text{MgH}_2(\text{CO}_3)_2$, and that the amounts of CaCO_3 and MgCO_3 carried by the two bicarbonate solutions, respectively, were not in sufficient concentration to serve as liberants.

EXPERIMENTAL

The results here offered were secured in a 5-year study of the potassium content of leachings from a loam treated with high-grade CaO and MgO, both in amounts equivalent to an application of 2,000 pounds and 3,750 pounds per 2,000,000 pounds of soil, and also with limestone and dolomite of 100-mesh fineness at the 2,000-pound-equivalent rate. The limestone contained 94.33 per cent CaCO_3 and 1.62 per cent MgCO_3 , while the dolomite contained 49.96 per cent CaCO_3 and 39.11 per cent MgCO_3 . In addition, both CaO and MgO were added at the 3,750-pound rate, and at the rate of 32 tons in conjunction with each of the three sulfur carriers— FeSO_4 , pyrite, and elementary sulfur—which were used also alone as controls. Each sulfureous material was added in an amount which carried sulfur at the constant rate of 1,000 pounds of S per 2,000,000 pounds of soil. The 3,750 pound CaO-equivalents of lime

and magnesia represented a 2,000-pound addition plus 1,750 pounds to care for the immediate acidity of FeSO_4 and the potential acidity of the pyrite and sulfur subsequent to their sulfofication, or chemical oxidation. The influence

TABLE 1

Potassium salts leached from "Cherokee" loam during a 5-year period—treatments of limestone and dolomite, alone and CaO , and MgO , with and without additions of FeSO_4 , pyrite and flowers of sulfur

TANK NUMBER	TREATMENT			POTASSIUM PER 2,000,000 LBS. OF SOIL									
	CALCIO-MAGNESIC			Annual period					5-year period				
	Material	CaO equivalent, per 2,000,000 lbs. of soil	Sulfur content of 1,000 lbs. per 2,000,000 lbs. of soil	First	Second	Third	Fourth	Fifth	Average annual	Total	Increase or decrease over no-treatment control		
				lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
50	None	None	None	11.8	8.4	12.7	7.0	6.2	9.2	46.1		
51	Limestone	2,000 lbs.	None	9.0	7.0	9.0	9.5	7.8	8.5	42.3	-3.8		
52	Dolomite	2,000 lbs.	None	7.4	5.5	9.6	8.5	4.1	7.0	35.1	-11.0		
53	CaO	2,000 lbs.	None	9.2	6.7	10.2	11.2	4.7	8.4	42.0	-4.1		
54	CaO	3,750 lbs.	None	5.6	6.8	11.6	7.5	4.1	7.1	35.6	-10.5		
55	MgO	2,000 lbs.	None	7.7	6.1	8.5	5.1	4.4	6.4	31.8	-14.3		
56	MgO	3,750 lbs.	None	8.5	6.3	9.8	8.9	4.2	7.7	37.7	-8.4		
57	None	None	FeSO_4	14.8	10.2	9.6	12.2	6.6	10.7	53.4	7.3		
58	CaO	3,750 lbs.	FeSO_4	6.0	7.3	10.2	7.7	4.5	7.1	35.7	-10.4		
59	MgO	3,750 lbs.	FeSO_4	5.3	5.7	15.4	8.3	3.3	7.6	38.0	-8.1		
60	CaO	32 tons	FeSO_4	5.4	5.3	14.6	5.5	4.9	7.1	35.7	-10.4		
61	MgO	32 tons	FeSO_4	10.3	4.4	6.9	4.2	2.3	5.6	28.1	-18.0		
62	None	None	Pyrite	11.6	10.6	11.3	10.8	6.6	10.2	50.9	4.8		
63	CaO	3,750 lbs.	Pyrite	6.5	10.8	8.1	7.5	5.2	7.6	38.1	-8.0		
64	MgO	3,750 lbs.	Pyrite	8.7	6.0	9.5	3.5	2.5	6.0	30.2	-15.9		
65	CaO	32 tons	Pyrite	6.4	7.0	9.6	8.8	5.1	7.4	36.9	-9.2		
66	MgO	32 tons	Pyrite	8.2	4.6	7.6	4.5	2.4	5.5	27.3	-18.8		
67	None	None	Sulfur	15.1	11.1	14.7	9.4	5.3	11.1	55.6	9.5		
68	CaO	3,750 lbs.	Sulfur	6.6	10.7	10.4	8.9	5.2	8.4	41.8	-4.3		
69	MgO	3,750 lbs.	Sulfur	12.7	7.7	8.6	7.6	3.5	8.0	40.1	-6.0		
70	CaO	32 tons	Sulfur	8.4	6.5	7.7	11.0	6.0	7.9	39.6	-6.5		
71	MgO	32 tons	Sulfur	8.0	3.5	7.4	3.6	2.3	5.0	24.8	-21.3		

of CaO and MgO upon the chemical and bacterial oxidative processes responsible for the formation of sulfates is reported in another contribution (8) now in the hands of the printer.

All treatments were mixed uniformly throughout the mass of soil. The soil used was secured from a near-by source and was protected to prevent drying after mixing and screening, and during the overnight determination of moisture. The soils were mixed and placed in 1/20,000-acre galvanized "ingot" iron, asphaltum-coated tanks, August 3, 1917, since which time they have been subjected to prevailing weather conditions. Each tank contains a sand filter-bed, from which runs a block-tin tube drainage outlet. This outlet passes through a reinforced concrete retaining wall and leads into the asphaltum-coated galvanized iron receptacles (6). As made necessary by distribution of rainfall, the leachings are collected, conveyed to the laboratory and after certain analyses on the separates are retained as aliquot-composites, acidified with HCl. At the end of each annual period the composites are analyzed for potassium by the colorimetric method of Schreiner and Failyer (9). The annual and total outgo of potassium from each of the 22 tanks for the years 1917 to 1922 are given in table 1.

DISCUSSION OF RESULTS

The amounts of potassium removed from the soil by leachings from natural rainfall were small. Nevertheless, certain consistent differences are shown. The results will be considered, however, on the basis of the total loss, with the detail of the annual losses left to the inspection of the interested student. However, the entire amount of leached potassium salts may not have been derived from the soil. Some potassium sulfate is precipitated in the rain-water at this point, as has been shown by MacIntire, Shaw and Young (7); but, this increment is a constant and will be considered as though native to the soil.

The total losses from both limestone and dolomite were less than the outgo from the control. The same was true also of the burnt lime and magnesia at both 2,000-pound and 3,750-pound rates. The two magnesia treatments show an average depression greater than that of the two lime additions. This is in harmony with previous findings (6) secured by the use of another soil.

The FeSO_4 group shows a decrease in outgo where the four lime and magnesia additions were made and an increase where FeSO_4 was added without a basic supplement. The augmented outgo of calcium and magnesium sulfates from the FeSO_4 acid-soil control and the absence of any FeSO_4 in the leachings demonstrated that the sulfate treatment was practically the same, primarily, as an equivalent treatment of sulfuric acid and, secondarily, as an equivalent of a mixture of CaSO_4 and MgSO_4 . Such a treatment would be expected to effect the liberation of potassic salts. But, if the leached potassium may be taken as a quantitative measure of the liberation effected, the 1,000 pound sulfate-sulfur addition, equivalent to 3,747 pounds of CaSO_4 , has liberated only 7.3 pounds of potassium, or a replacement ratio of 1:0.00195, as representing the full effect over the 5-year period. However, only 934.6 pounds of sulfate sulfur, or 719.9 pounds in excess of that in the rainfall, has been recovered

during the full 5-year period, 534.3 pounds having been leached during the first year. Practically the full recovery of the sulfate radical was obtained during the first year, where the heavy MgO supplement was incorporated and recoveries of 82.9 per cent and 92.4 per cent were obtained from the 3,750-pound CaO and MgO additions, respectively. Thus it appears that the liberative action of the calcium and magnesium sulfates evidenced in the FeSO₄ acid soil control was either prevented or repressed by a secondary action of the added excess of the two alkali-earths. In other words, the more concentrated solutions of soil-derived sulfates with a minimum of calcium and magnesium bicarbonates gave an increased outgo of potassium salts; but, solutions of even greater concentration of calcium and magnesium sulfates with an increase in respective bicarbonates proved depressive to potassium outgo. As applied to two of our residual soils, this constitutes cumulative evidence to the effect that the *bicarbonates of calcium and magnesium are depressive rather than inactive in their influence upon the outgo of potassium*. It may be that the two alkali-earths are responsible for the formation of hydrated oxides of iron, and possibly of aluminum, and that through adsorption these two products, retard the potassium outgo in the free soil-water leachings.

In another contribution now in print (8), we have shown that the oxidation of pyrite, as evidenced by sulfate outgo, was more rapid in the control than in the four tanks to which lime or magnesia was added. The pyrite treatment therefore represents a progressive ferrous sulfate addition. In like manner, in corresponding restricted measure, the four CaO and MgO additions with pyrite represent treatments of CaSO₄ and MgSO₄, respectively, with the bicarbonates in larger quantities, and these show a distinct retardative effect upon potassium outgo. In this series, as was true also of the FeSO₄, and elementary sulfur group, the heavy MgO treatment proved the most depressive of the five conditions.

In the contribution above mentioned, it is shown that the sulfate outgo from the unsupplemented addition of sulfur was almost as rapid as that from the FeSO₄ control and it is therefore not surprising to find that the increase in potassium outgo from the sulfur alone was as great as that from the added sulfate. As differing from the pyrite group, however, the light lime and both light and heavy magnesia additions accelerated the generation and outgo of sulfates from the additions of sulfur. Nevertheless, in spite of the more rapid and greater ultimate outgo of calcium and magnesium sulfates from the specified treatments of this series, the excess of bicarbonates again proved to be depressive to the sulfate outgo, as was the case in the FeSO₄ parallel.

These findings, as a whole, demonstrate that calcic and magnesian oxides are depressive to potassium outgo when the two materials are used in economic and practical amounts, as well as in excess, and that the same proves true of 100-mesh limestone and dolomite in chemical equivalence and at the rate ordinarily used. The results do not prove, however, that the alkali-earth treatments would serve as deterrents to the assimilation of potassium by

plants of such extensive root development as the clovers. For, the basic treatments activate the flora which generate nitrates and sulfates and the enhanced supplies of these nutrients and the development of a favorable soil reaction would so stimulate the young plants as to cause a spread of their root growth, thus increasing their ability to forage for the needed potassium.

Calcium and magnesium losses are not given. It was found, however, that soil-derived calcium and magnesium sulfates appeared coincidently with increases in potassium leachings from the unlimed tanks. It is not proved that this result is due to the liberation of potassium through basic interchange.

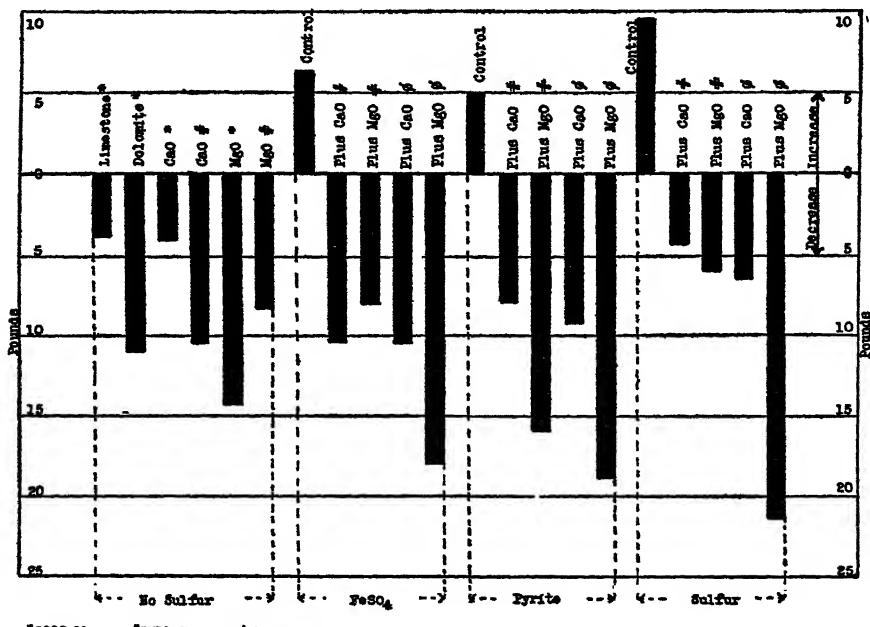


FIG. 1. INCREASE OR DECREASE IN 5-YEAR POTASSIUM OUTGO AS CAUSED BY CALCIC AND MAGNESIC TREATMENTS OF CHEMICAL EQUIVALENCE

Variation from base line shows pounds of potassium per 2,000,000 pounds of soil.

But, assuming that the small increases in potassium outgo from the non-basic treatments were due to basic interchange, and that there was no extensive readsorption by the soil, the increase in soluble potassium would represent only a fraction of the amount which would ordinarily be applied as a fertilizer.

SUMMARY

A study of the leaching of potassium from a 23-unit lysimeter equipment during a 5-year period is reported in this paper. The influence of calcic and magnesic materials upon the liberation of potassium from the soil was deter-

mined by additions of limestone, dolomite, CaO and MgO in chemical equivalence, at the rate of 2,000 pounds of CaO per 2,000,000 pounds of soil. Both CaO and MgO were used also at an equivalent rate of 3,750 pounds. Five treatments each of FeSO₄, pyrite, and elementary sulfur also were used, four of each set receiving supplements of lime or magnesia each at two rates.

The results show that every form and rate of calcic and magnesian treatment, alone and in conjunction with sulfates, was depressive to the outgo of potassium. Increases over the control were obtained in the three cases of sulfur carriers when un-supplemented by either alkali-earth, but such increases were found to represent only a minute fraction of the theoretical liberation to be accredited to the amounts of calcium and magnesium sulfates derived from the sulfureous treatments.

REFERENCES¹

- (1) BROWN, B. E., AND MACINTIRE, W. H. 1911 The relation of certain water-soluble soil constituents in plots 16-14. *In* Penn. State Col. Ann. Rpt. 1910-11, p. 105.
- (2) LIPMAN, C. B., AND GERICKE, W. F. 1918 Does CaCO₃ or CaSO₄ affect the solubility of the soil's constituents? *Univ. Cal. Pub. Agr. Sci.*, v. 3, no. 10, p. 271.
- (3) LYON, T. L., AND BIZZELL, J. A. 1918 Lysimeter Experiments: I. N. Y. (Cornell) Agr. Exp. Sta. Mem. 12, p. 7-115.
- (4) LYON, T. L., AND BIZZELL, J. A. 1921 Lysimeter Experiments: II. N.Y. (Cornell) Agr. Exp. Sta. Mem. 41, p. 71.
- (5) MACINTIRE, W. H. 1912 Results of thirty years of liming. *In* Penn. State Col. Ann. Rpt. 1911-12, p. 73.
- (6) MACINTIRE, W. H. 1919 The liberation of soil potassium induced by different calcic and magnesian materials, as measured by lysimeter leachings. *In* Soil Sci., v. no. 5, p. 337-397.
- (7) MACINTIRE, W. H., AND YOUNG, J. B. 1923 Sulfur, calcium, magnesium and potassium content and reaction of rainfall at 10 points in Tennessee. *In* Soil Sci., v. 15, no. 3, p. 205-227.
- (8) MACINTIRE, W. H., SHAW, W. M., AND YOUNG, J. B. 1923 Influence of calcic and magnesian treatments upon sulfate leachings from soil alone and with additions of ferrous sulfate, pyrite and sulfur. *In* Soil Sci., v. 16, p. 159-182.
- (9) SCHREINER, O., AND FAILYER, G. H. 1906 Colorimetric, titration, and turbidity methods. U. S. Dept. Agr. Bur. Soils Bul. 31, p. 31-33.
- (10) TRESSLER, D. K. 1918 The solubility of soil potash in various salt solutions. *In* Soil Sci., v. 6, no. 3, p. 237-257.
- (11) WHEELER, H. J. 1910 Studies of the needs of Rhode Island soils. *In* R. I. Agr. Exp. Sta. Bul. 139, p. 75.

¹Since preparation of this manuscript, a related article has been contributed by D. E. Haley, *In* Soil Sci., v. 15, no. 3, p. 167.

THE ABSORPTION OF IONS BY PLANTS

D. R. HOAGLAND¹

College of Agriculture, University of California

Received for publication June 18, 1923

INTRODUCTION

The absorption of ions from the soil solution and their functions in the plant must always be regarded as among the most important problems of soil and plant interrelations. It is not sufficient to study only the soil and its dissolved components; the plant must likewise receive consideration, if we are to understand the whole chemical system involved in plant growth. It is essential to such an understanding to learn something of the processes by which ions are absorbed from culture media. To what extent does one ion influence the absorption of another ion? How is absorption affected by the reaction and by the concentration of the solution? What is the relation between the intake of solutes and of water? These questions illustrate the nature of the discussion upon which we are now entering.

Considerable attention has previously been given in this laboratory to the question of the absorption of inorganic solutes by plants at different stages of growth. The methods of soil, sand and solution cultures have all been employed at various times. These experiments have been continued under simplified conditions for the purpose of obtaining data bearing more directly on the relative absorption of different ions, and on related questions.

The course of absorption must generally be followed with the aid of chemical analysis applied either to the culture solution or to the plant tissues, and the data so obtained do not necessarily represent degrees of cell permeability, as has been pointed out by Osterhout (12) and by Brooks (1). The determination by chemical methods of the intake of ions by higher plants, it will readily be granted, does not always offer the most favorable means of approach to the study of the chemistry of the plant cell. It appears essential, nevertheless, to carry out such investigations from the point of view of the relations existing between a plant and its culture medium. Otherwise we have no basis for the interpretation of many experiments bearing on important problems of plant nutrition. Meanwhile, it is confidently to be expected that researches of the type recently reported by Loeb (10), Osterhout (14), and other physiologists, will eventually enable us to overcome some of the difficulties now constantly confronting the investigator of plant metabolism.

¹ The writer desires to acknowledge the invaluable assistance of Mr. J. C. Martin, Instructor in Plant Nutrition, in connection with a portion of the analytical work.

A considerable number of experiments dealing with the absorption of essential and non-essential elements by plants have been described, among which may be noted those of Pantanelli (15), Waynick (20), and recently, of Redfern (16). The general literature has been discussed by these investigators and no attempt will be made in this article to review the many citations. It does not appear, however, that the investigations so far reported have been definitely planned to answer certain questions the discussion of which forms the main purpose of the present paper. In many of the previous investigations, the analytical control was incomplete, and the number of plants used too small. The importance of hydrogen-ion concentration was, of course, not known to the earlier workers.

Before discussing the data pertaining to the removal of ions from solution, it is desirable to make a statement dealing with the changes of hydrogen-ion concentration produced by the growth of plants. It was shown in earlier work that complete culture solutions containing nitrate tended to have their reaction changed in the direction of the neutral point. Under the experimental conditions then adopted, it was also observed that no considerable increase of acidity occurred when plants were grown in single salt solutions. Later and more extensive experiments have shown that the growth of barley and pea seedlings may produce in the solutions of certain salts, e.g., K_2SO_4 and $(NH_4)_2SO_4$, an intensity of acidity which may be accompanied by injury to the plant, after sufficient lapse of time. This phase of the work is discussed in another article in more detail, but the pH values of the solutions used in these experiments are included in a number of the tables.

The object of the first series of experiments was to determine the effect of a positively charged ion on the absorption of an ion of opposite charge, and vice versa. Numerous series of solutions were used, in some cases keeping the cation the same and in others the anion. Equivalent concentrations of salts were chosen so that in each set of cultures, the common ion would be present in the same concentration in all the solutions. The magnitudes of the total concentrations were similar to those found in ordinary culture solutions and in soil solutions.

EXPERIMENTAL TECHNIQUE

In each experiment the plants were first grown during a preliminary period in a complete culture solution and then the entire group of cultures was divided into uniform sets of either 49 or 98 plants. The tumblers which were used as culture vessels had a capacity of 120 cc. and seven plants were placed in each tumbler. Before transferring the plants to the new solutions, the roots were thoroughly rinsed with distilled water. The periods over which the absorption of ions was measured were, in most cases, limited to 2 or 3 days. At the end of these periods, the plants were removed and the residual solutions were analyzed. The tops of the plants from each set of cultures were weighed green, and in some instances the dry weights of tops and of roots also were recorded. Barley, of the Beldi variety, or Four Thousand, was used in all experiments. The time allowed for absorption from the special solutions was made brief, since if plants are grown for longer periods in different solutions, pronounced variations in their size and stage of development may occur and these variations

may complicate any interpretation of the results. It is obvious, also, that single salts or simple mixtures of salts cannot serve for extended periods of growth. Our intention was to attempt a comparison of the relative absorption of ions from different solutions by plant systems as nearly alike as possible.

In the majority of the experiments, distilled water was added to the cultures at intervals so as to maintain the volumes of solution approximately constant; in other experiments, no water was added to make up for loss by transpiration, and the solutions were analyzed without dilution. This technique was adopted when it was desired to compare the relative absorption of water and of ions.

Care was taken to prevent the creeping of solution up to the cotton which held the plants in place in the cork. By the time the plants were ready for study, the stems usually almost completely filled the holes in the corks, so that the cotton could be removed, otherwise new pieces of cotton were inserted and kept dry.

The plants were grown on a balcony with full exposure to sunlight, at different seasons of the year. The preliminary periods referred to above were generally about three weeks in length, but varied according to weather conditions. The complete culture solution in which the plants were started was similar to that used for many years in this laboratory and which has been found to permit of excellent development of many types of plants. Ordinarily, only two portions of this solution were supplied, since it was the intention to prevent, as far as possible, any excess absorption of ions during the first period. In all cases, the plants had a very thrifty appearance, and possessed excellent root systems.

The amounts of ions removed from the solutions were determined by chemical analysis rather than by conductivity measurements. While the latter method is far less laborious, and has yielded results of interest in the hands of True and Bartlett (19) it is obviously not capable of a definite interpretation in terms of individual ions or chemical elements which is one of the most interesting aspects of the question. The analytical methods were those long employed in this laboratory for the examination of soil extracts and culture solutions. Complete analyses of many of the solutions made it possible to take into consideration, not only the ions originally present, but those given off by the plant roots, whether as a result of leaching from dead cells, or of exchange of ions in the cell wall or protoplasm. Complete analyses also possess the advantage that equivalents of positive and negative ions may be balanced and the accuracy of the work checked. While such complete analytical data were obtained in many experiments, in order to conserve space, only the most significant figures are given here. All the values have been calculated in terms of milli-equivalents (reaction values).

Whenever a complete analysis was made and the positive and negative ions values compared, it was found that the agreement was within the limits of error generally recognized as permissible in the analysis of solutions of this type.

The comparatively large number of plants used lessened any errors of variability. No importance is attached to any but very considerable differences in the quantities of ions absorbed. Frequently duplicate experiments were made and the results agreed in all instances within limits of much smaller magnitude than those considered as significant for our present purposes. Since determinations of the absorption of ions by individual plants in the large number experimented with could not be made, the data for absorption are, of course, not amenable to statistical treatment. In two typical experiments the dry weights of individual cultures (each made up of 7 plants) were obtained and the probable error of the mean calculated. This was found to be about 6 per cent, which is similar to the values found by Davis (4) for various sets of wheat plants grown in different culture solutions. Assuming that the variability in absorption of ions by individual plants is of the same order of magnitude as that of dry weights, the differences considered significant in the present paper are greater than those assignable to variability. For these various reasons, it is justifiable to believe that the factor of variability does not enter into the conclusions which are drawn.

With regard to the possible toxicity of single salt solutions, it may be noted that the plants showed no evidence of injury, and this would scarcely be expected, considering the brief duration of the contact between the plants and the solutions, and the low concentration of the latter. Moreover, after barley plants have been growing in a complete culture solution for some time, they may later continue to grow in single salt solutions for considerable periods without injury. Injurious hydrogen-ion concentrations were not developed under the experimental conditions.

ABSORPTION OF POTASSIUM FROM DIFFERENT SALTS

Turning now to a consideration of the data presented in table 1, we find marked variations in the amounts of potassium absorbed which are dependent upon the anion in equilibrium with the potassium ion. The greatest absorption occurred from the solution of potassium nitrate, the least absorption from the solution of potassium sulfate. Potassium was absorbed to a decidedly greater extent from the chloride than from the sulfate solution. In this experiment potassium and chlorine ions were absorbed in practically equivalent quantities. No such equivalence of absorption was found with the other salts. Potassium ions were removed from solution in greater equivalent quantity than sulfate, phosphate, or bicarbonate ions, while the absorption of nitrate ions was nearly double that of potassium ions, the former being replaced in the solution by bicarbonate ions. In the case of potassium sulfate, the solution became slightly more acid, and also calcium and other ions, derived from the roots, replaced potassium to a certain extent.

ABSORPTION OF CALCIUM AND MAGNESIUM FROM DIFFERENT SALTS

The experiments carried out with calcium salts (table 2) gave evidence of approximately equivalent absorption of cations and of anions from solutions of either calcium sulfate or calcium phosphate. From the chloride and nitrate solutions, the anion was removed in significantly larger quantity than the cation. The equivalents of nitrate removed were about six times those of calcium. It is very interesting to observe that chlorine ions, as well as nitrate ions could be replaced in the solution by bicarbonate ions.

Two salts of magnesium were studied, nitrate and sulfate (table 3). The nitrate was absorbed in greater equivalent amounts than magnesium, while sulfate was removed from solution to a lesser extent than magnesium. In each case, there was a tendency for the hydrogen-ion concentration to decrease. The magnesium nitrate solution became almost neutral.

ABSORPTION OF NITRATE FROM DIFFERENT SALTS

In another series of cultures, four different nitrate solutions of the same concentration of NO_3^- were compared (table 4). In every case, NO_3^- ions were removed to a much greater extent than the respective cations. The reactions

of the solutions were changed to approximate neutrality. The disproportion between the absorption of anions and cations is greater with calcium and magnesium nitrates than with sodium and potassium nitrates.

TABLE I

NAME OF SALT	INITIAL CONCENTRATION	IONS ABSORBED BY PLANT		IONS ENTERING SOLUTION			AGE OF PLANTS	LENGTH OF ABSORPTION PERIOD
		K	Anion	Ca	Mg	HCO ₃		
	atm.			<i>milli-equivalents</i>			days	days

Experiment 1A

K_2SO_4	{	6.60	1.44		0.50	0.53	}	28	2
		6.60	1.57		0.50	0.49			
KCl	{	6.48	2.67	2.40	0.38	0.44	0.68		
		6.48	2.57	2.51	0.47	0.45	0.82		

Experiment 2

K_2SO_4	6.32	0.74	0.40	0.32	0.24		25	1½
KCl	6.32	1.28	1.30	0.24	0.18	0.36		
KNO_3	6.45	1.66	3.19	0.19	0.21	1.89		
KH_2PO_4	6.32	0.90	0.14	0.28	0.21			
KHCO_3	6.30	1.20	0.84	0.24	0.20			

NAME OF SALT	INITIAL CONCEN-TRATION	K ION ABSORBED BY PLANT	REACTION		H ₂ O ABSORBED	AGE OF PLANTS	LENGTH OF ABSORPTION PER OD
			Initial	Final			
am.	milli-equivalents		pH	pH	cc.	days	days

Experiment 3

KCl and CaCO_3 suspension.....	6.22	1.74	6.3	6.3	550	35	2
K_2SO_4 and CaCO_3 suspension.....	6.22	1.12	6.3	5.8	540		

Experiment 4

KCl and CaCO_3 suspension.....	6.20	0.91	6.9	6.8	610	19	1
K_2SO_4 and CaCO_3 suspension.....	6.22	-0.02	6.9	6.8	670		

TABLE 2

Absorption of ions from solutions of different calcium salts

NAME OF SALT	INITIAL CONCENTRATION atm.	IONS OBSERVED BY PLANT		IONS ENTERING SOLUTION			REACTION Initial pH	H_2O ABSORBED cc.	AGE OF PLANTS days	LENGTH OF ABSORPTION PERIOD days
		Ca	Anion	K	Mg	HCO_3				
		milli-equivalents								

Experiment 1

CaCl ₂	4.90	0.73	0.13	0.48					21	3
	4.90	0.83	2.06	0.11	0.34	1.26				
Ca(NO ₃) ₂	4.90	1.21	4.50	0.07	0.38	3.44				
	4.90	1.25	4.54	0.12	0.44	3.69				

Experiment 2

CaCl ₂	12.50	1.50	2.37	0.02	0.28	1.12	5.8	6.6	625	
Ca(NO ₃) ₂	12.70	1.66	5.48	0.09	0.20	4.12	5.6	7.0	510	
Ca(H ₂ PO ₄) ₂	12.30	1.03	0.95	0.20	0.27		4.2	4.2	590	
CaSO ₄	12.30	0.88	0.83	0.09	0.20	0.32	6.4	6.6	715	

Experiment 3

CaSO ₄	4.59	0.00	0.00	0.04	0.16	0.47	6.6	6.0	510	
Ca(NO ₃) ₂	4.89	0.60	3.41	0.08	0.07	3.08	6.0	7.0	470	

Experiment 4

CaCl ₂	12.30	2.40	3.19		1.10	6.8	710			
CaCl ₂	61.70	5.70	7.24		1.30	6.8	440			

TABLE 3

*Absorption of ions from solutions of different magnesium salts**

NAME OF SALT	INITIAL CONCENTRATION atm.	IONS ABSORBED BY PLANT		IONS ENTERING SOLUTION			REACTION		H_2O ABSORBED cc.
		Mg	Anion	Ca	K	HCO_3	Initial pH	Final pH	
		milli-equivalents							
Mg(NO ₃) ₂	21.1	4.75	5.40	0.70	0.03	2.48	5.0	6.7	130
MgSO ₄	20.7	1.82	1.17	0.60	0.06	0.08	5.0	5.3	135

* Age of plants was 28 days. Length of absorption period was 2 days.

ABSORPTION OF POTASSIUM AND SODIUM FROM THE CHLORIDES AND SULFATES

The significant difference between the chloride and sulfate solutions in the amount of potassium removed seemed to be of sufficient interest to merit additional experimentation. In two experiments, the procedure was varied by adding a small quantity of calcium carbonate in suspension to the solutions of potassium salts (table 1, exp. 3 and 4). This prevented the increase of hydrogen-ion concentration consequent upon the more rapid absorption of potassium than sulfate. An appreciable concentration of calcium was also maintained in these solutions. The same result was obtained as before, that is, the potassium was absorbed from the chloride solution to a significantly greater extent than from the sulfate solution.

TABLE 4
*Absorption of ions from solutions of different nitrate salts**
(All values calculated in terms of milli-equivalents)

NAME OF SALT	INITIAL CONCENTRATION	IONS ABSORBED BY PLANTS		IONS ENTERING SOLUTION				REACTION		H ₂ O ABSORBED	
		NO ₃	Cation	milli-equivalents				Initial	Final		
				M	Mg	Ca	HCO ₃				
	atm.							pH	pH	cc.	
Ca(NO ₃) ₂	3.96	1.64	0.41	0.17	0.26		1.60	6.8	7.2	370	
KNO ₃	3.90	2.58	1.03		0.28	0.24	1.76	6.0	7.2	430	
Mg(NO ₃) ₂	3.98	2.33	0.39	0.20		0.37	2.18	5.4	7.2	435	
NaNO ₃	4.14	2.06	1.55	0.39	0.24	0.28	1.48	6.6	7.0	410	

* Age of plants was 19 days. Length of absorption period was 2 days.

Other experiments were made in which sodium salts were used, instead of potassium salts (tables 5 and 6). Here, also, the removal of cations from the sulfate solution was definitely smaller than from either the chloride or the bicarbonate solutions. In one experiment, sodium chloride and sulfate were mixed in equivalent quantities and the absorption of ions determined. The quantity of sodium removed was approximately the same as in the case of the chloride solution alone, but the removal of sulfate was apparently depressed by the presence of chlorine ions, since the percentage of sulfate removed was decreased and that of chlorine increased.

Referring to the solutions of sodium salts, sodium and chlorine were absorbed in practically equivalent quantities, but a greater number of equivalents of sodium than of sulfate were removed (a similar relation was observed between potassium salts). This discrepancy between the absorption of cations and anions is accounted for only partially by the change of reaction in the solution, but a somewhat greater displacement of calcium and potassium from the root tissues occurred in case of the sulfate.

TABLE 5
*Absorption of ions from solutions of different sodium salts**

NAME OF SALT	INITIAL CONCEN-TRATION	IONS ABSORBED BY PLANT		IONS ENTERING SOLUTION				REACTION		H ₂ O ABSORBED
		Na	Anion	C ^a	K	Mg	HCO ₃	Initial	pH _{final}	
atm.		<i>milli-equivalents</i>								
NaCl.....	10.70	2.78	2.75	0.30	0.13	0.25	0.75	6.2	6.4	670
	10.70	3.17	3.12	0.27	0.06	0.25	0.62	6.2	6.4	720
Na ₂ SO ₄	10.87	1.78	0.99	0.40	0.24	0.29		5.0	4.2	660
	10.87	1.82	1.01	0.37	0.27	0.25		5.0	4.0	730
NaHCO ₃	11.48	2.17	1.80	0.13	0.13	0.16		7.9	7.8	680
	11.48	2.00	1.80	0.03	0.13	0.16		7.9	7.8	690

* Age of plants was 17 days. Length of absorption period was 2 days.

TABLE 6
Absorption of ions from solutions of different sodium salts

NAME OF SALT	CONCEN-TRATION	IONS ABSORBED BY PLANT				AGE OF PLANT	LENGTH OF ABSORPTION PERIOD
		Na	Cl	SO ₄	HCO ₃		
atm.		<i>milli-equivalents</i>					
NaCl.....	10.57	1.91	2.36			31	4
	10.57	2.09	2.56				
Na ₂ SO ₄	11.09	0.82		0.66			
	11.09	0.82		0.81			
NaCl plus Na ₂ SO ₄	11.31	1.91	1.83	0.25			
	11.31	1.96	2.03	0.23			
NaHCO ₃	11.09	1.35			1.00		
	11.09	1.35			1.05		

ABSORPTION OF CHLORINE FROM DIFFERENT SALTS

One series of experiments was planned to determine the absorption of chlorine ions, when these were associated with different cations, calcium, sodium potassium and magnesium (table 7). No notable difference was observed, although the greatest quantity of chlorine was removed from the potassium chloride solution. The equivalents of potassium and of chlorine removed were similar, but the equivalents of chlorine absorbed were significantly greater than those of calcium or magnesium. Bicarbonate ions formed in the solution maintained the equilibrium between positive and negative ions.

TABLE 7
*Absorption of ions from solutions of different chloride salts**

NAME OF SALT	INITIAL CONCENTRATION	IONS ABSORBED BY PLANT		IONS ENTERING SOLUTION				H_2O ABSORBED
		Cl	Cation	Ca	Mg	K	HCO_3	
<i>atm.</i>								
KCl.....	6.32	1.97	2.05	0.60	0.20		0.64	560
MgCl ₂	6.22	1.83	1.33	0.60		0.16	1.16	550
	6.22	1.72	1.22	0.75		0.16	1.12	595
CaCl ₂	6.37	1.69	0.80		0.18	0.22	1.20	600
	6.37	1.58	0.60		0.16	0.13	1.20	555
NaCl.....	6.32	1.64	1.97	0.60	0.16	0.31	0.72	575
	6.32	1.52	1.89	0.75	0.26	0.23	0.76	555

* Age of plants was 28 days. Length of absorption period was 2 days.

ABSORPTION FROM PHOSPHATE SOLUTIONS

In a test of several phosphate solutions of similar concentrations of phosphate, equivalent absorption of anions and cations did not occur, calcium and magnesium being removed in smaller quantity than phosphate, and potassium in greater quantity (table 8). The amounts of phosphate removed from the different solutions were nearly the same, but the absorption was not sufficiently great in this series to warrant any exact comparisons. The decrease of hydrogen-ion concentration in the potassium phosphate solution was evidently caused by small amounts of bicarbonates derived from the roots.

TABLE 8
*Absorption of ions from solutions of different phosphate salts**

NAME OF SALT	INITIAL CONCENTRATION	IONS ABSORBED BY PLANT		IONS ENTERING SOLUTION			REACTION		H_2O ABSORBED
		PO ₄	Cation	K	Mg	Ca	Initial	Final	
<i>atm.</i>									
Ca(H ₂ PO ₄) ₂	2.67	0.45	0.25	0.22	0.12		3.7	5.6	395
KH ₂ PO ₄	2.73	0.43	0.62		0.22	0.37	4.7	5.3	455
Mg(H ₂ PO ₄) ₂	2.71	0.44	0.17	0.20		0.47	4.0	5.4	385
NaH ₂ PO ₄	2.81	0.42		0.41	0.24	0.32	4.7	5.4	475

* Age of plants was 19 days. Length of absorption period was 2 days.

FURTHER STUDIES OF CALCIUM ABSORPTION

Additional studies were then made with calcium chloride, sulfate and nitrate. The results are given in table 2, experiments 3 and 4. The general results of the previous experiment were confirmed. In this instance, no determinable

absorption of sulfate occurred from the calcium sulfate solution, which was of lower concentration than before. Since calcium ions are apparently removed very slowly when in equilibrium with sulfate ions, it was decided to determine what would occur when nitrate ions were added (as potassium nitrate) to a solution of calcium sulfate. This addition of nitrate caused an increased absorption of calcium. While the total quantities involved were small, the difference noted was considerably beyond the limits of analytical error.

GENERAL CONSIDERATIONS

All of the results of the experiments which have just been under consideration are consistent in showing that one ion can exert a definite influence on the absorption of another ion of opposite charge. It also appears that calcium, sulfate, and possibly magnesium ions are less readily removed from solution by barley plants than chlorine, potassium and nitrate ions. These same relations are found when plants are grown for long periods in culture solutions, such as those used by the writer. Under these conditions, calcium, magnesium and sulfate may be left in the solution in considerable quantity at the end of the period of growth, when all or nearly all of the nitrate, phosphate and potassium have been removed. In certain other experiments, not now reported, with Shive's solution, as well as that used by the writer, there was evidence that when solutions were changed at weekly intervals, no absorption of calcium, magnesium, or sulfate took place during certain periods, although potassium and nitrate were absorbed in appreciable amounts at all periods.

Some of the interrelations of cations in the processes of absorption have been considered in another paper (7), but one of the conclusions should be stated here. It was discovered that an effective concentration of sodium (0.1 M to 0.3 M) decreased the rate of absorption of calcium, magnesium and potassium. In the same way, potassium can influence the absorption of calcium. These facts illustrate the necessity for considering the possible inhibiting effect of one cation on another, at least within certain concentrations. A number of experiments bearing on this point are summarized in table 9. These data show quite definitely that sodium and potassium ions may be absorbed in appreciable quantities at the same time that calcium leaves the plants roots, so as to increase the concentration of this element in the solution. If the concentration of calcium is sufficiently high, however, absorption rather than excretion may take place. These experiments, supported by others reported elsewhere, clearly suggest that sodium and potassium ions may exert a depressing effect on the absorption of calcium ions.

The experiments so far under consideration were made with plants which were first grown in a complete culture solution and then transferred to single salt solutions. A number of other experiments were carried out in which the seedlings were placed in the solution to be studied immediately after germination. The data obtained by this procedure (table 10) show that the relative

rates of absorption of the different ions were very similar to those observed in the previous experiments.

The preceding statements bring up the question of the total capacity of a plant to remove ions from solution during a given period. To what extent is the absorption affected by the amounts of the ions already taken up by the

TABLE 9
Effect of sodium and potassium salts on absorption of calcium

NAME OF SALT	INITIAL CONCENTRATION		Ca ABSORBED OR EXCRETED	Na ABSORBED	AGE OF PLANTS	LENGTH OF ABSORPTION PERIOD
	Ca	Na or K				
	atm.	atm.				
<i>Experiment 1</i>						
CaCl ₂	4.90		1.00			
CaCl ₂ -NaCl.....	4.60	43.0	-0.10	4.82	25	1
CaCl ₂ -NaCl.....	4.60	43.0	-0.45	4.74		
<i>Experiment 2</i>						
CaCl ₂ -NaCl.....	4.59	43.1	0.60	5.50	21	3
<i>Experiment 3</i>						
CaCl ₂ -NaCl.....		34.8	-0.55			
CaCl ₂ -NaCl.....	3.40	34.8	0		21	2
CaCl ₂ -NaCl.....	6.30	34.8	0.70			
CaCl ₂ -NaCl.....	13.00	34.8	0.80			
CaCl ₂ -NaCl.....	25.40	34.8	1.60			
<i>Experiment 4</i>						
CaCl ₂ -NaCl.....	0.85	0.87	-0.45	0.43	25	2
CaCl ₂ -NaCl.....	4.20	4.35	-0.15	0.96		
CaCl ₂ -NaCl.....	9.20	9.50	0.50	1.22		
CaCl ₂ -NaCl.....	16.80	17.40	0.80	1.65		
<i>Experiment 5</i>						
CaCl ₂ -KCl.....	0.04	0.66	-0.75	0.47	26	2
CaCl ₂ -KCl.....	0.15	2.64	-0.22	0.99		
CaCl ₂ -KCl.....	0.31	5.30	-0.31	1.45		
CaCl ₂ -KCl.....	0.78	13.20	-0.21	1.97		

plant? The following experiment bears on this point (table 11). A large set of barley seedlings was started in the usual manner in a complete culture solution and after a period of 10 days the solution was changed in the case of one half of the plants, while the other half was allowed to remain in the original solution. After 8 additional days of growth, all the plants received a change of solution and the absorption was then measured over a period of 2 days, according to

TABLE 10

*Increase or decrease of concentration of ions in various solutions as a result of absorption by barley plants**

	COMPLETE CULTURE SOLUTION								CaCl ₂ SOLUTION		
	K	Ca	Mg	NO ₃	PO ₄	SO ₄	HCO ₃	Reaction	Ca	Cl	Reaction
	milli-equivalents								milli-equivalents		
Initial concentration	2.26	9.48	4.85	10.38	1.13	4.98		pH	5.19	4.9	4.9
Final concentration	0.45	12.18	6.16	6.99	0.63	6.90	4.27	6.8	3.99	3.61	5.2
Concentration at end in percentage of original concentra- tion.....	20.0	129.0	127.0	67.0	56.0	139.0			77.0	73.0	

	CaSO ₄ SOLUTION			Ca(NO ₃) ₂ SOLUTION			KNO ₃ SOLUTION			KNO ₃ + Ca(NO ₃) ₂ SOLUTION		
	Ca	SO ₄	Reaction	Ca	NO ₃	Reaction	K	NO ₃	Reaction	Ca	K	NO ₃
	milli- equivalents	milli- equivalents	pH	milli- equivalents	milli- equivalents	pH	milli- equivalents	milli- equivalents	pH	milli- equivalents	milli- equivalents	pH
Initial concentra- tion.....	7.08	7.07	5.4	6.23	5.58	5.2	4.51	4.89	5.0	2.60	4.47	7.08
Final concentration	5.99	5.83	4.0 (?)	3.79	1.69	6.6	0.31	0.10	5.4	1.20	0.24	0.19
Concentration at end in per- centage of orig- inal concentra- tion.....	85.0	32.0		61.0	30.0		7.0	2.0		46.0	5.0	3.0

* Plants placed in solutions immediately after germination. Period of absorption 15 days.
No additional water was added during this period.

TABLE 11

*Effect of preliminary treatment on absorption of ions during a given period**

	K	Ca	Mg	NO ₃	PO ₄	SO ₄	REACTION	REMARKS
	milli-equivalents	milli-equivalents	milli-equivalents	milli-equivalents	milli-equivalents	milli-equivalents	pH	
Initial concentration.....	4.80	9.1	4.93	12.4	1.28	4.7	5.4	
	(1.77)	14.1	7.97	12.1	1.52	8.0	6.8	1 preliminary portion of culture solution
Final concentration.....	0.69	13.6	7.80	9.0	1.43	7.5	6.8	2 preliminary portions of culture solution

* No water was added during experimental period. Age of plants was 18 days and length of absorption period, 2 days.

the plan already described. The plants which had the initial change of solution were slightly larger, but smaller amounts of several ions were absorbed by these plants than by those receiving but one portion of solution. While these facts cannot be interpreted in terms of a definite chemical equilibria between the plant cells and the solution, it is plain that the rates at which ions can be absorbed may tend to decrease as a plant increases its content of these ions. The application of any simple chemical equilibria to these processes is obviously of doubtful practicality. The growth and multiplication of cells makes it impossible to subject systems of such complexity to any rigid analysis in this regard, at least in the present state of our knowledge.

EFFECT OF CONCENTRATION ON ABSORPTION

The next consideration which is logically suggested concerns the effects of concentration on the absorption of ions. This is a phase of the inquiry which will require long extended investigation. One experiment can be presented now which may indicate one or two of the chief points involved. A series of solutions of KNO_3 plus $\text{Ca}(\text{NO}_3)_2$ of seven different concentrations was prepared with the potassium and calcium present in the same proportion in all solutions. Barley plants were transferred to these solutions after two weeks of growth. During the brief experimental period, no water was added to the cultures since it was desired to ascertain how the solutions would become adjusted when they were left undisturbed. The total absorption of water was noted. The results are shown in the form of three graphs (fig. 1). In each case, the solid lines indicate the actual concentration of the ion in question at the end of the period of absorption, and the dotted lines represent the increase of concentration which would have occurred if no ions had been removed by the plants. In the two lowest concentrations, the solutions have become more dilute with respect to nitrate, in the next higher concentration no change has taken place (that is, water and nitrate have been absorbed in equal proportion), while in the four solutions of highest original concentration, the residual solutions have increased in concentration, and the line for residual concentration approaches more closely to that for transpiration effect. A very similar condition was found in the case of potassium, except that only one solution became diluted. A much smaller proportion of calcium than of potassium or nitrate was absorbed and the two lines are close together. In one of the lower concentrations, calcium left the roots, instead of being absorbed.

This experiment, as well as others including several reported in an earlier paper (5), all lead to the conclusion that a much greater proportion of the total quantity of readily absorbable ions present in the solution is removed from solutions of low concentration. It follows from these statements that a plant possesses considerable ability to adjust itself to culture media of different concentrations.

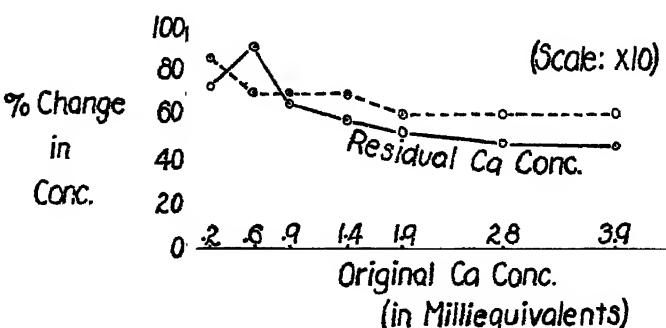
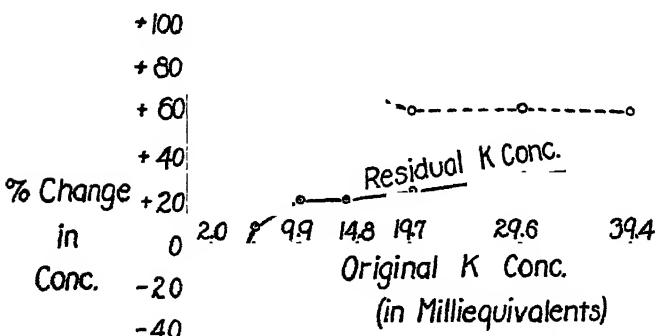
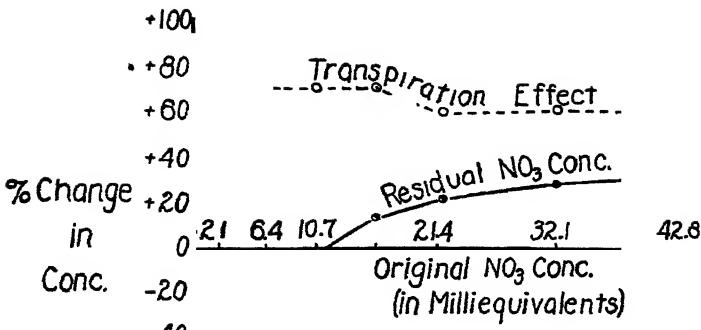


Fig. 1. ABSORPTION OF IONS FROM SOLUTIONS OF KNO_3 AND $\text{Ca}(\text{NO}_3)_2$ OF DIFFERENT CONCENTRATIONS

Upper dotted line shows concentration which would have been produced by simple evaporation of water equal in amount to transpiration. Lower line indicates actual concentration of solution at end of absorption period (26 hours). Plants were 19 days old.

RELATION OF ABSORPTION OF IONS TO ABSORPTION OF WATER

The relation of the intake of water to the intake of inorganic solutes has been a subject for speculation and experimentation from early times. It has been variously stated that the absorption of essential elements is entirely dependent on transpiration and that it is independent of the latter process. Careful quantitative experiments seem to be lacking in most cases. In a recent article by Muenscher (11), the literature of this subject is reviewed and additional data are presented. These refer chiefly to ash analyses, and so do not permit of any conclusions with reference to individual elements. It was shown, however, that in general, there was no correspondence between transpiration of water and ash content of plants.

In the present investigation, two methods of attack were adopted, first the reduction of transpiration by placing plants under bell jars (so arranged as to provide access of air) and second, the study of the effect of plants on the concentration of different ions in culture solutions, when no additional water was added during the course of the experiment. In other words, the relative absorption of ions and of water by the plants determined the change in the composition of the solution. One experiment of this type has just been described. In the majority of trials by the first method, the reduction in transpiration was not associated with anything like a proportionate decrease in the absorption of ions, although there was a general tendency for decreases in transpiration to be accompanied by decreases in the quantities of ions absorbed. In these experiments in which transpiration was reduced by placing the plants under bell jars, the conditions for growth or for metabolism (for example, the carbon dioxide supply) also may have been less favorable, which makes it very difficult to decide to what extent transpiration *per se* influenced absorption of ions. The data cited in table 13 show that in one experiment the solution from the plants kept in the open became less concentrated with respect to several ions than the solution from the plants placed under bell jars, even though in the former case the transpiration of water was nearly double.

It was thought that a more direct idea of the comparative intake of water and of inorganic elements might be obtained by allowing the solution to remain undisturbed during the brief period of the experiment. At the end of the periods, the solutions were analyzed without dilution. This simple procedure yielded some rather interesting results, which are reported in tables 10 and 12. The complete culture solutions became more concentrated with respect to certain ions, and more dilute with respect to others. The ions which regularly increased in concentration were Ca, Mg and SO₄. K and NO₃ ions were removed from solution more rapidly than water. The phosphate was increased in concentration under some circumstances, and under other circumstances decreased. The resultant effect on the culture solutions was that their composition was completely altered in a very short time. The nature of the alteration in the complete culture solution may be summarized as follows: Decrease in concentration

of K and NO₃ ions, increase of concentration of Ca, Mg and SO₄ ions, increase of HCO₃ ions, decrease in hydrogen-ion concentration. When growth and transpiration are restricted by placing seedlings in incomplete culture solutions, after a sufficient period of time, a decrease of concentration of Ca and SO₄ may also take place, as indicated in table 10. The different behavior of the three anions, NO₃, SO₄, and Cl, all in equilibrium with K ions, is illustrated in table 12.

Later an attempt was made to study the changes in the composition of a culture solution during a succession of very brief intervals. For this purpose, 80 culture vessels were used with a total of 560 plants. Samples of 5 cc. were taken from each of the culture vessels and united into composite samples, which were analyzed. No additional water was added during the time of the experi-

TABLE 12
*Increase or decrease of concentration of various anions in equilibrium with K ions**

	K	NO ₃	SO ₄	Cl	HCO ₃	REACTION
<i>milli-equivalents</i>						
Initial concentration.....	19.6	5.1	10.6	4.96		pH 5.2
Final concentration.....	24.9	0.9	15.9	5.64	4.64	6.9
Concentration at end in percentage of original concentration.....	127.0	18.0	149.0	114.0		

* No water added during experimental period. Age of plants was 18 days and length of absorption period, 2 days.

TABLE 13
*Increase or decrease of concentration of ions under conditions of reduced transpiration**

	K	Ca	Mg	NO ₃	PO ₄	SO ₄	H ₂ O ABSORBED
<i>milli-equivalents</i>							
Initial concentration.....	4.55	8.0	4.4	11.4	1.26	7.2	
Final concentration.....	1.51	12.5	7.3	9.5	0.44	18.5	505
Final concentration (under bell jar) ...	3.15	9.6	5.2	9.7	1.43	13.1	265

* Age of plants was 19 days and length of absorption period, 2 days.

ment. The results as plotted are shown in figure 2. It is clear that the absorption of the different ions did not follow the same course. Again, it was found that the solution became more concentrated with respect to Ca, Mg and SO₄ ions, while the concentrations of K and NO₃ ions decreased. In this experiment, the PO₄ ion remained at approximately its original concentration. The sum of the equivalents of anions absorbed was greater than that of cations, bicarbonate ions being formed in the solution to maintain the equilibrium.

The effect of light was studied in one preliminary experiment (table 14). The usual technique was followed, except that during the absorption period, part of the plants were left in the light, and part placed under conditions of darkness. Of course, this involved a considerable difference in the amounts of water transpired. The concentration of all the ions, except K and PO₄ was

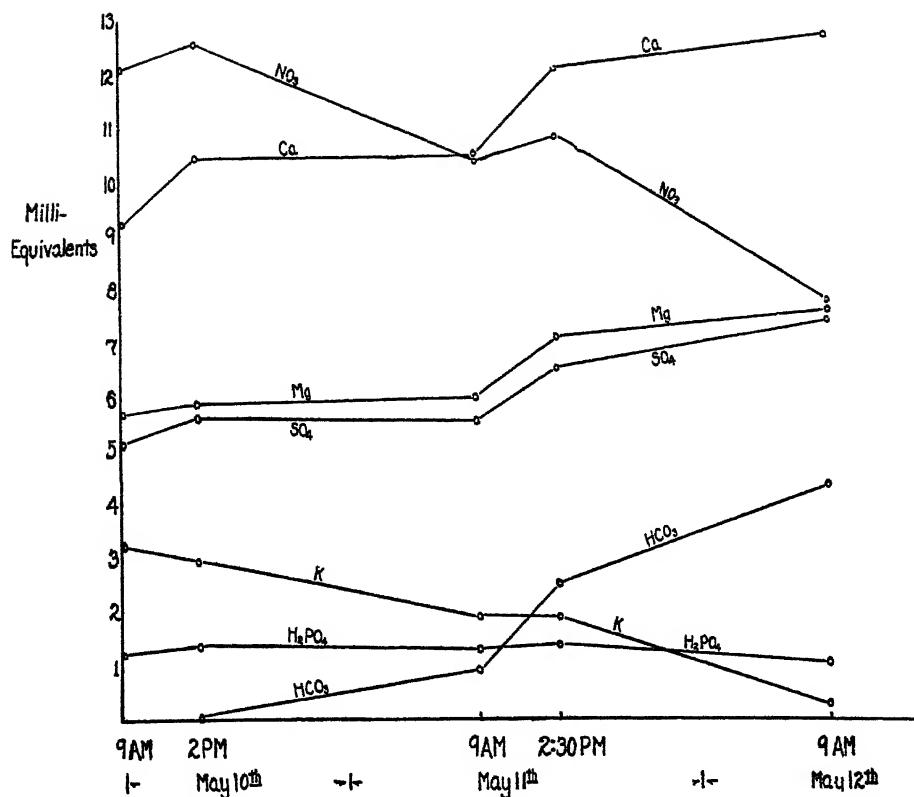


FIG. 2. CHANGE OF COMPOSITION OF COMPLETE CULTURES SOLUTION AT VARIOUS INTERVALS OVER A PERIOD OF 48 HOURS

Plants were 19 days old.

TABLE 14
*Effect of light on absorption of ions**
(All values calculated in terms of milli-equivalents)

ION	CONCENTRATION IN LIGHT		CONCENTRATION IN DARK	
	Initial	Final	Initial	Final
NO_3^-	10.5	10.9	10.5	8.1
SO_4^{--}	4.7	8.8	4.7	5.4
PO_4^{--}	1.3	0.04	1.3	0.70
Ca^{++}	8.7	11.8	8.7	9.1
Mg^{++}	5.2	9.3	5.2	5.9
K^+	4.4	1.2	4.4	1.7

* No water was added during the experimental period; 1090 cc. was absorbed in the light while 435 cc. was absorbed in the dark.

increased to a greater extent in the light than in the dark. In the case of the two ions mentioned, there was a decrease of concentration in the light, although more water was transpired. It seems probable that metabolic processes in which light was a factor, affected the rate of absorption of certain ions. Of course, from present information, no definite prediction of influence of light on absorption can be made for any particular case, since undoubtedly the stage of growth and previous nutritional history of a plant will be important factors. In other experiments, for example, nitrate ion might also decrease in concentration.

DISCUSSION

In discussing in a more general way the results presented in this paper, we may conclude first that the processes of absorption have to do with ions. All the data we have obtained are in favor of this conclusion. Comber (3) in a recent article suggests that plants do not behave in soils as they do in solution cultures, in that they may absorb colloidal substances directly from the soil, or at least that diffusion may proceed through a continuous colloidal system formed by the intimate union of root hairs and soil particles. While this may be a possibility, it seems quite feasible to meet Comber's objections to soil solution theories. This point, however, will be discussed in another paper.

While it may appear probable that absorption processes are concerned with ions, it certainly should not be assumed that the ions are acting as completely independent units. On the contrary, as we have shown, one ion influences the absorption of another and in a complete culture solution, the complexity of conditions so far defies any really satisfactory analysis from the standpoint either of the chemist or of the plant physiologist. It does not appear, however, that anything is to be gained by interpreting the results of solution culture experiments in terms of salt proportion. In solutions of the dilution with which we are concerned, a high percentage of dissociation must exist. The actual analysis of such solutions must be made on the basis of ions or of chemical elements, and it is obvious that the results of absorption studies can best be expressed in these terms. Moreover, the interpretation of the data must almost necessarily be made in terms of ions or chemical elements.

Pantanelli (15) drew the general conclusion from his absorption studies that the two ions of a salt are seldom removed from solution in equal proportion, which conclusion is, on the whole, in accord with the data presented herein, although Pantanelli did not determine the extent to which an exchange of ions accounted for the discrepancies in the absorption of the different ions. Redfern (16) investigated the absorption by barley of calcium and chlorine ions from calcium chloride solutions. She found that calcium was absorbed in excess and other bases entered into solution. Our own results indicated that chlorine was absorbed by barley more rapidly than calcium. The difference between these two results can possibly be explained by the fact that the concentrations of solution used by Redfern were greater than our own. We have found in one

experiment with $MgCl_2$ that at a low concentration chlorine was absorbed more rapidly than magnesium, while at a relatively high concentration magnesium was removed to a greater extent than chlorine.

The replacement of one ion by another in a culture solution is a condition of any extensive inequality in the absorption of positively and negatively charged ions, since the change of hydrogen-ion concentration which can occur is comparatively limited. The notable example of replacement is, of course, that of NO_3^- ions by HCO_3^- ions. The ease with which this can occur makes it possible for NO_3^- ions to be absorbed to a far greater extent than most cations. As already stated, the same type of replacement can occur with the chlorine ions, but to a much more limited extent. While the selective absorption of NO_3^- has long been known, it does not appear that any one has advanced any really satisfactory explanation of the mechanism involved. In our earlier work, we held the view that positive and negative ions are either absorbed in equal proportion or else that an exchange of ions occurs. In the light of present knowledge, however, it is difficult to say whether, for example, K may be absorbed from K_2SO_4 as KOH, or whether the K ion may replace the H ion directly to the limited extent which corresponds to the increase of hydrogen-ion concentration taking place in the solution. When an alkaline solution is used and the hydroxylion concentration of the solution decreased, it is possible that HCO_3^- ion is involved in the selective absorption of bases.

It may be presumed that the rapid reduction which nitrate undergoes in the plant has something to do with its absorption, but this type of explanation would not answer for potassium which may also be absorbed with great rapidity. Experiments to be mentioned presently suggest that potassium occurs in plants largely in dissociated form.

The exchange of one base for another which seems to occur in root cells under certain conditions has been explained by True (18) as being attributable to reactions in the calcium pectate middle lamella. He emphasizes the importance of calcium in making other ions physiologically available. There can be no doubt that calcium is essential to the preservation of the normal permeability of plant cells, as has long been known from the work of Osterhout and others (14). It might be suggested, however, in the application of these facts to explain the absorption of ions by plants over extended periods of time, that an inadequate supply, not only of calcium, but of any essential element obviously will render the other elements present unavailable, since the plant will be unable to grow to any extent. It is often true, however, that lack of calcium may inhibit growth more quickly than lack of any other element. Different types of plants differ greatly in this respect. Barley seedlings grow well for some time and produce good root systems in solutions of KNO_3 (0.005 M concentration) without calcium, except that derived from the seed. Pea seedlings, on the other hand, grow well in solutions of calcium nitrate, but are soon injured by potassium nitrate. In the experiment with barley referred to in table 10, it does not appear that calcium in ordinary concentration had much effect on the absorption of potassium.

Another point of great interest is involved in the relative rates of penetration of different ions. Why, for example, is the SO_4 ion usually absorbed so much more slowly than other ions? It is not apparent that there is any simple relation between the ordinary chemical and physical properties of the ions and their rates of penetration into plant cells. Stiles (17) was unable to show any correlation between the rates of diffusion of SO_4 and Cl ions into gels and into living cells. It is quite apparent that not only the chemical characteristics of the ion, but also those of the cell membrane must be taken into consideration.

Certain other aspects of the problem of the absorption of ions by plants have been discussed elsewhere, but for the sake of completeness, a brief reference to the conclusions may be made at this point. Investigations (2, 8, 9, 13) on the fresh water alga *Nitella* from which cell sap may be obtained practically or entirely uncontaminated, have shown that most of the inorganic elements of the sap exist in dissociated form, and not chemically combined with organic substances. The cells contain ions in concentrations far higher than those of the media in which the plants grow. An expenditure of energy is apparently involved in the processes of penetration of ions into the cell sap. As possibly bearing on this relation, Davis and the writer have found (8) that Cl and other ions are not absorbed by *Nitella* to any extent except when the cells are exposed to light.

In the experiments reported in this paper, very brief periods of absorption were considered, but even in these brief periods, growth and metabolism were undoubtedly active, and the absorption of ions which occurred during the periods in question cannot be dissociated from these processes. The point of view which it is sought to suggest here is entirely different from that which assumes any simple type of chemical equilibrium between the plant and its culture medium. It cannot be doubted that the plant cell operates in accordance with the laws of chemistry and physics, but the system is a dynamic one, and the energy relations of the chemical reactions taking place are, as yet, unknown.

Possibly the initial event in the removal of an ion from solution may involve some sort of chemical combination between the ion and a constituent of the cell wall or protoplasm. It was observed in connection with the experiments on *Nitella* (8) that nitrate ions penetrate more readily from an acid solution than from an alkaline one. Evidence is also available from experiments on barley plants to show that from an alkaline solution cations are absorbed to a greater extent than anions, the hydroxyl-ion concentration being decreased (6). Perhaps some of these facts will suggest the applicability of Loeb's (10) recent researches on proteins, but in this connection it must be considered that it is possible for cations to be removed from solution more rapidly than anions, even when the reaction is acid, for example, in the case of potassium sulfate. It is also probable that compounds other than proteins play a part in the mechanism of absorption.

Finally, it must be very emphatically stated that the absorption of ions by a plant depends not only upon the culture solution, but upon conditions of light,

temperature, and humidity, and therefore it cannot be expected that any two experiments will give identical results, unless every condition is the same. Any experiments of the type described in this paper are useful only in so far as they throw some light on the general principles of ion absorption.

SUMMARY

1. Determinations were made of the absorption of ions by barley plants from numerous solutions of single salts or simple mixtures of salts, as well as from complete culture solutions. Absorption was generally determined over very brief periods. Large numbers of plants were employed and comparisons were made between uniform sets of plants several weeks old.

2. Different ions were absorbed at different rates, but definite evidence was obtained of the significant influence of one ion on the absorption of another. All three types of relations were involved, cation to anion, cation to cation, and anion to anion.

3. The slowly absorbed sulfate ion decreased the rate of absorption of associated cations; thus potassium was absorbed much more rapidly from the nitrate or the chloride than from the sulfate. Similar relations were found between the ions of various other salts.

4. The presence of a relatively high concentration of sodium decreased the rate of absorption of other cations, particularly potassium and calcium.

5. During a given period the proportion absorbed from the total quantity of easily absorbable ions present decreases as the concentration of these ions in the solution decreases. In this way, plants can adapt themselves, to a considerable extent, to solutions of low concentration.

6. Ions are seldom removed from solution by the plant in the same proportion as water. Under some circumstances K, NO₃ and PO₄ ions may be removed from solution at a far greater rate than water. At the same time, Ca, Mg and SO₄ ions may be removed less rapidly than water. Therefore, as the plant absorbs water and ions, the same solution may become more dilute with respect to certain ions and more concentrated with respect to others.

7. The importance of climatic conditions as affecting absorption of ions is emphasized. One experiment is described in connection with the influence of light on absorption.

8. Attention is called to the fact that energy exchanges are involved in the processes of absorption. Permeability relations alone are inadequate to explain these phenomena in the living plant.

REFERENCES

- (1) BROOKS, S. C. 1917 Methods of studying permeability of protoplasm to salts. *In Bot. Gaz.*, v. 64, p. 230-249.
- (2) BROOKS, M. M. 1922 The penetration of kations into living cells. *In Jour. Gen. Physiol.*, v. 4, p. 347.
- (3) COMBEE, N. M. 1922 The availability of mineral plant food. A modification of the present hypothesis. *In Jour. Agr. Sci.*, v. 12, p. 363-369.

- (4) DAVIS, A. R. 1921 The variability of plants grown in water cultures. *In* Soil Sci., v. 11, p. 1-32.
- (5) HOAGLAND, D. R. 1919 Relation of the concentration and reaction of the nutrient medium to the growth and absorption of the plant. *In* Jour. Agr. Res., v. 18, p. 73-117.
- (6) HOAGLAND, D. R. 1923 The effect of the plant on the reaction of the culture solution. Univ. of Calif. Agr. Exp. Sta. Tech. Paper (In press).
- (7) HOAGLAND, D. R. 1923 The effects of salts on the intake of inorganic elements and on the buffer system of the plant. Univ. of Calif. Agr. Exp. Sta. Tech. Paper (In press).
- (8) HOAGLAND, D. R., AND DAVIS A. R. 1923 The composition of the cell sap of the plant in relation to the absorption of ions. *In* Jour. Gen. Physiol., v. 5, p. 629-646.
- (9) IRWIN, M. 1923 The behavior of chlorides in the cell sap of *Nitella*. *In* Jour. Gen. Physiol., v. 5, no. 4, p. 427-428.
- (10) LOEB, J. 1922 Proteins and the Theory of Colloidal Behavior. McGraw Hill Book Co., New York.
- (11) MUENSCHER, W. C. 1922 Effect of transpiration on absorption of salts by plants. *In* Amer. Jour. Bot., v. 9, p. 311.
- (12) OSTERHOUT, W. J. V. 1917 Does the temperature coefficient of permeability indicate that it is chemical in nature? *In* Bot. Gaz., v. 63, p. 317-320.
- (13) OSTERHOUT, W. J. V. 1922 Some aspects of selective absorption. *In* Jour. Gen. Physiol., v. 5, no. 2, p. 225-230.
- (14) OSTERHOUT, W. J. V. 1922 Injury, Recovery, and Death, in Relation to Conductivity and Permeability. J. B. Lippincott Co., Phila. and London.
- (15) PANTANELLI, E. 1915 Über Ionenauaufnahme. *In* Jahresb. Wissen Bot. v 56, p. 689-733.
- (16) REDFERN, G. M. 1922 On the absorption of ions by the roots of living plants. *In* Ann. Bot., v. 36, p. 167-174.
- (17) STILES, W. 1921 The penetration of electrolytes into gels. IV. The diffusion of sulphates in gels. *In* Biochem. Jour., v. 15, p. 629-635.
- (18) TRUE, R. H. 1922 The significance of calcium for higher green plants. *In* Science, n. s., v. 55, p. 1-6.
- (19) TRUE, R. H., AND BARTLETT, H. H. 1916 The exchange of ions between the roots of the *Lupinus Albus* and culture solutions containing three nutrient salts. *In* Amer. Jour. Bot., v. 3, p. 47-57.
- (20) WAYNICK, D. D. 1918 The chemical composition of the plant as further proof of the close relation between antagonism and cell permeability. *In* Univ. of Calif. Publ. Agr. Sci., v. 3, p. 135-219.

PARTIAL STERILIZATION OF SOIL, MICROBIOLOGICAL ACTIVITIES AND SOIL FERTILITY: II¹

SELMAN A. WAKSMAN AND ROBERT L. STARKEY

New Jersey Agricultural Experiment Stations

Received for publication June 25, 1923

The preliminary results presented in the first paper (16) have demonstrated that treatment of soil with volatile antiseptics and heat has an important influence not only upon the development of bacteria and protozoa, but also upon the soil actinomycetes and especially the soil fungi. The metabolism of soil fungi is of such a nature that by it we can explain readily the phenomena observed as a result of partial sterilization of the soil.

Among the chief disadvantages which present themselves in working with field soils is their great variability, both in regard to chemical composition and numbers of microorganisms, the large number of various environmental conditions influencing the numbers and activities of bacteria and the fact that the previous course of microorganisms in the particular soil, as far as numbers and activities are concerned, is unknown. Also, it was recognized that the determination of ammonia formation alone in the soil is not a reliable index of the activities of bacteria, first, because ammonia accumulation in the soil is subject to too many variables (15) and, second, because the fungi which develop rapidly in partially sterilized soil may either accumulate large quantities of ammonia or assimilate it and convert it into microbial protein, depending upon the amount of available energy in the soil and species of fungi developing as a result of partial sterilization.

An experiment was, therefore, carried out as follows:

One-kilogram portions of a uniform, air-dried, sieved Sassafras loam soil were placed in a series of sixty 1-quart glazed earthenware pots and the proper amount of moisture was added, amounting to 20 per cent of the weight of the soil (60 per cent of total moisture-holding capacity). The pots were then covered with glass plates and placed in the incubator at 25-28°C. Every 10 to 14 days, the soils were brought to weight by the addition of distilled water. At various intervals, 6 pots were sampled for the determination of nitrates and bacterial numbers. Samples were taken by means of a clean cork borer (about 1 cm. in diameter) to a depth of 3-4 inches from various parts of the pot. At the same time six of the pots were also placed in the respirator apparatus and the amount of carbon dioxide evolved, using a constant aeration for 14 days, was determined. The respiration was carried on at constant temperature (25-28°C.). At the end of the 14 days, the pots were taken out and covered again. The soils were otherwise undisturbed. These determinations of

¹ Paper No. 138 of the Journal Series, New Jersey Agricultural Experiment Stations, Department of Soil Chemistry and Bacteriology.

numbers of bacteria, actinomycetes and fungi, nitrate content and CO₂-producing capacity were continued until the changes became hardly noticeable within a brief period of time. For this a period of about 11 months was required. This procedure was followed in order to obtain a soil in which the history of microbial changes was known, a soil which had been brought to a definite level of activities (we may call it microbial balance or unstable equilibrium, as far as this term can be applied to microbial activities).

The different determinations made upon this undisturbed soil, when plotted, give us the courses of the changes of the microorganisms in the soil as indicated by the total numbers developing on the plate, nitrate accumulation and evolution of carbon dioxide. These curves are given in figure 1.

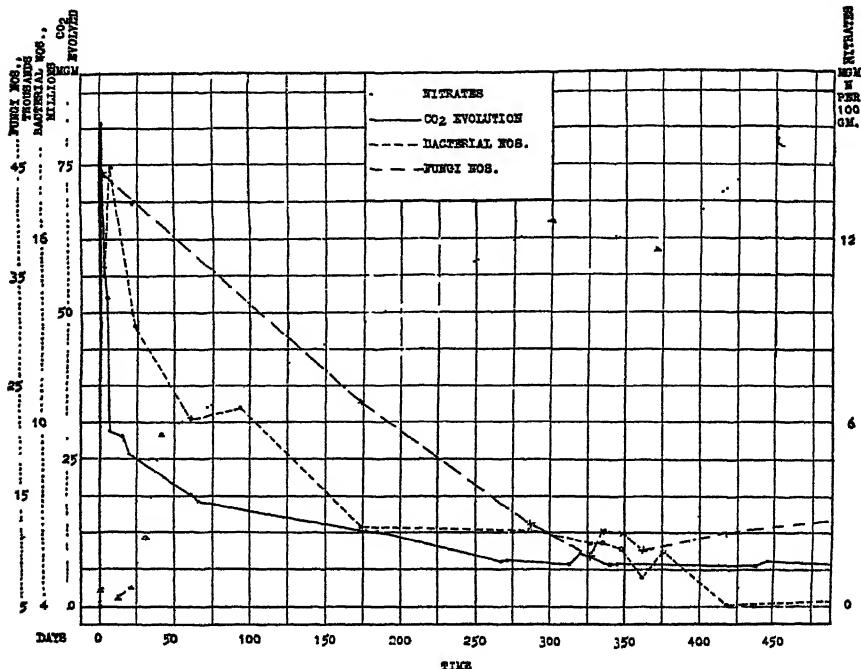


FIG. 1. COURSE OF BIOLOGICAL ACTIVITIES IN UNDISTURBED SOIL

In view of the fact that the soil was air-dried before it was properly mixed and distributed in the pots, there is a decided increase in the numbers and activities of microorganisms, soon after moistening. In the case of bacteria, the maximum is obtained only after 3 or 4 days. This is followed by a drop in numbers, at first rapidly, then more slowly, so that after 175 days the numbers of bacteria and actinomycetes have come to a certain level at which the decrease in numbers is only very slow. The fungi reach their maximum soon after moistening and are then followed by a gradual decline, much less abrupt than in the case of bacteria and actinomycetes, and a certain level is reached only after about 250 days. The ratio of actinomycetes to the

total number of microorganisms developing on the plate declines with the increase in bacterial numbers, then increases with the decrease in the numbers of bacteria developing on the plate, till a constant ratio is attained, namely till about 20 to 25 per cent of the organisms, exclusive of fungi, developing on the plate are actinomycetes.

The rate of evolution of carbon dioxide reaches a maximum during the first 24 hours after moistening the soil, then it falls off very rapidly, reaching also a certain level after about 150 days. The more precipitous fall in the rate of evolution of carbon dioxide than the numbers of bacteria has been observed previously by Fischer (3) and others. Fischer explained this by the low respiratory power of the bacteria after they reached the maximum development, although they are still capable of developing into colonies on the plate. This phenomenon will be dwelt upon at greater length elsewhere. The nitrate content of the soil increases at first slowly, then rapidly, till a certain maximum nitrate content is attained, equivalent to about 10 mgm. of nitrate nitrogen in 100 gm. of soil. The curve in the case of nitrate accumulation in the soil is an autocatalytic curve, which has been previously pointed out by Miyake (10).

Eleven months after the soils were started, the numbers of microorganisms did not change appreciably. At this point a uniform balance of microbiological activities had become established, as indicated by the unchanging rate of CO_2 production. At this time the 60 pots of soil were divided into 16 groups, 3 or 6 pots in each group, and the soil in each pot was submitted to various treatments, as indicated below:

1. Remained untreated, to serve as control.
2. Soil was taken out from the pots, mixed thoroughly and placed in the pots again.
3. Soil was removed, well mixed with 0.5 per cent CaO , and returned to pots.
4. Soil was removed, well mixed with 1 per cent CaCO_3 , and returned to pots.
5. Soil was spread out in large open glass dishes in incubator and allowed to air-dry for 14 days, then returned to original pots and brought back to original weight by addition of sterile distilled water.
6. Soils were treated as in group 5, but were reinoculated with 0.5 per cent of fresh soil (untreated soil from one of the control pots).
7. Soil from each pot was transferred to individual bottles, 1 per cent of toluene was added and bottles closely stoppered. After 48 hours, the soil was spread out for 3 hours to allow the toluene to evaporate; then it was returned to the original pot and sterile water added to bring back to weight.
8. Same as treatment 7, only reinoculated with 0.5 per cent of fresh soil.
9. Soil treated with 1 per cent of carbon bisulfide in a manner similar to the toluene treatment.
10. Same as treatment 9 but reinoculated with 0.5 per cent fresh soil.
11. Pots with soil placed in hot water, until soil temperature in center of pot reached $65^{\circ}\text{C}.$, and kept at that temperature for 1 hour.
12. Same as treatment 11, but reinoculated with 0.5 per cent of fresh soil.
13. Soil removed from pots, 0.2 per cent of ground dry alfalfa hay was added to each and well mixed with the soil.
14. Soil removed from pots, 0.05 per cent of sulfur was added to each and well mixed in.

TABLE I
*Influence of soil treatment upon the activities of protozoa**

TREATMENT	AFTER 14 DAYS			AFTER 28 DAYS			AFTER 42 DAYS			AFTER 104 DAYS		
	C†	F	A	C	F	A	C	F	A	C	F	A
Control.....	+++†	+++†	++	++	+++	++	++	++	++	++	++	++
Mixed.....	++	++	++	+	++	+	++	++	++	++	++	++
CaO.....	0	0	0	0	0	0	0	0	0	0	0	0
CaCO ₃	+	++	++	++	++	++	++	++	++	++	++	++
Air dried.....	0	++	0	++	++	++	++	++	++	++	++	++
Air dried and fresh soil.....	0	++	0	++	++	0	++	++	++	++	++	++
Toluene.....	0	0	0	0	0	0	0	0	0	0	0	0
Toluene and fresh soil.....	0	++	0	++	++	0	++	++	++	++	++	++
CS ₂	++	++	++	++	++	++	++	++	++	++	++	++
CS ₂ and fresh soil.....	0	0	0	++	++	0	++	++	++	++	++	++
Steamed.....	++	++	++	++	++	0	++	++	++	++	++	++
Steamed and fresh soil.....	0	0	0	++	++	0	++	++	++	++	++	++

* Protozoa were determined by adding 1 cc. of a 1:20 dilution of the soil to two flasks each containing 50 cc. of the sterile media (hay infusion and soil extract).

† C = ciliates, F = flagellates, A = amoebae;

+= few, ++ = many, +++ = very many.

‡ Few flagellates after 14 days of air-drying.

15. Soil removed from pots, 200 mgm. of K_2SO_4 and 200 mgm. $CaHPO_4$ was added to each and well mixed in.

16. Same as treatment 15, with 250 mgm. of $NaNO_3$ in addition.

All the pots were then covered with glass plates and kept at optimum moisture in the incubator room. Since there was only enough room in the respirator for the study of CO_2 evolution from 12 soils at any one time and the period used was 14 days, the treatments were so arranged as to permit care of all the pots. At various intervals samples of soil were taken for the study of numbers of bacteria, fungi and protozoa, as well as nitrate content. Ammonia was determined only after prolonged incubation periods. The CO_2 -production by the variously treated soils was also determined at various intervals. The results are presented in figures 2-16 while table 1 gives a record of the occurrence of protozoa.

EFFECT OF TILLAGE

The mere mixing of soil, without allowing it to air-dry, resulted only in a slight stimulating effect as indicated by the carbon dioxide production (fig. 2). However, there was a depression in bacterial numbers. The protozoa were not affected. The fungi were at first depressed, then stimulated; the depression was accompanied by a reduction in nitrate content. Is it possible that the mere tilling of the soil, which means thorough aeration, resulted in the germination of the fungus spores with the development of a fungus mycelium? This might temporarily indicate a reduction in numbers followed by an increase when spore formation takes place. If that were the case, we could easily explain the assimilation of nitrate by the growing mycelium, increase in CO_2 production and reduction in bacterial numbers.

INFLUENCE OF TREATMENT WITH CALCTUM OXIDE

The addition of 0.5 per cent CaO had a decided sterilizing effect upon the microbial population of the soil, as shown in figure 3. In view of the fact that the pots were placed in the respirator soon after the addition of the lime and kept in a CO_2 -free atmosphere for 2 weeks, there was not enough of the CO_2 to carbonate the CaO. This accounts for the fact that no CO_2 is formed at first. It is also indicated by the very high alkalinity of the soil ($pH = 9.6 +$). The depression of CO_2 production was accompanied by a depression in the numbers of bacteria and fungi. However when the pots were exposed to the atmosphere and carbonation took place, there was a rapid increase in the numbers of microorganisms and CO_2 production. The protozoa were destroyed as a result of the treatment. But after 28 days large numbers of ciliates, flagellates and amoebae were found in the soil. This particular period coincided with the maximum development of bacteria and fungi as well as the maximum rate of CO_2 evolution. The rapid development of microorganisms brought about a decrease in the amount of nitrate in the

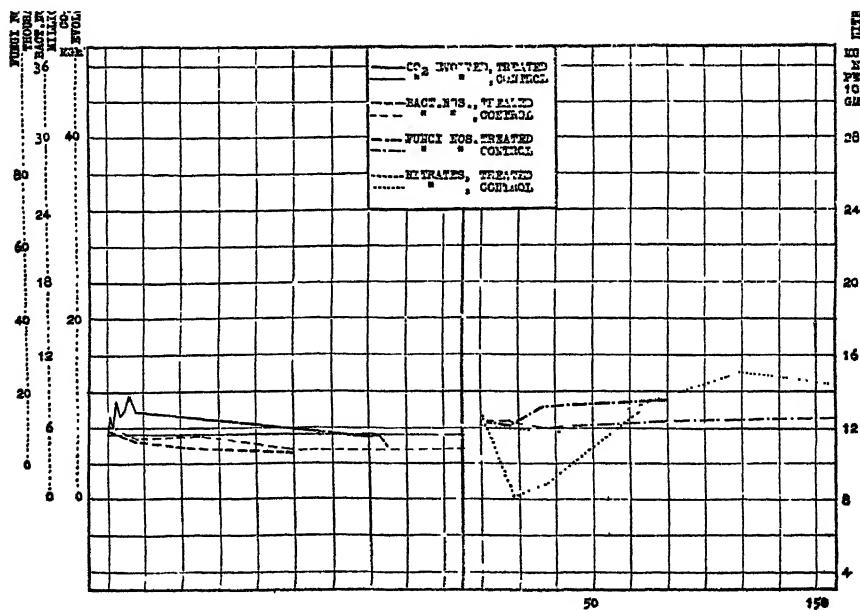


FIG. 2. INFLUENCE OF TILLAGE ON BIOLOGICAL ACTIVITIES IN SOIL

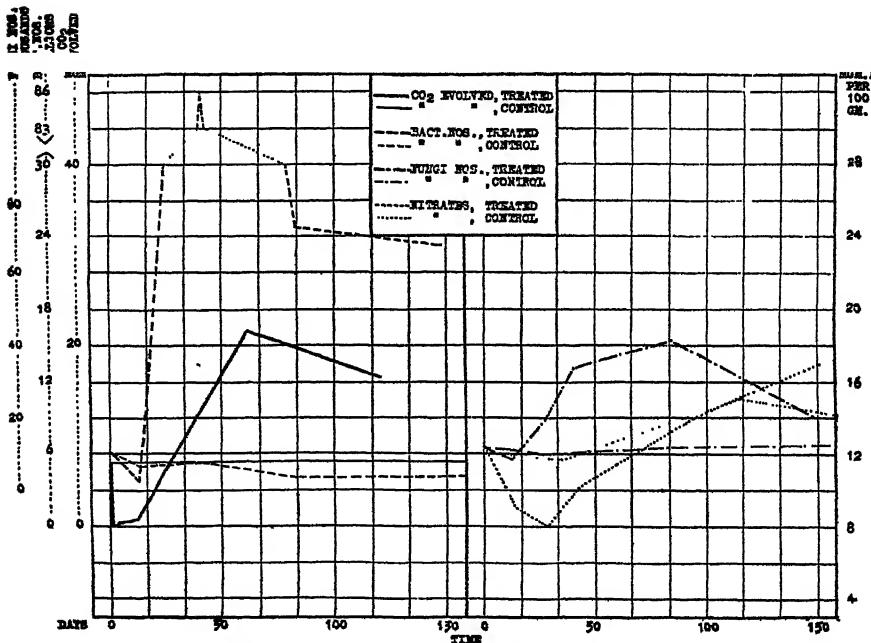


FIG. 3. INFLUENCE OF CaO ON BIOLOGICAL ACTIVITIES IN SOIL

soil, but as soon as the numbers of CO_2 production began to decline, an increase in the nitrate accumulation took place, so that in 150 days the amount of nitrate (16.9 mgm.) was higher than in the control. The soil contained only traces of ammonia, about 1 mgm. in 100 gm. of soil.

The influence of CaO upon the development of bacteria in the soil has been pointed out by various investigators. We need but refer to the work of Fischer (3), Hutchinson (5) and Miller (9). Fischer found that the addition of small quantities of CaO (0.1–0.3 per cent) brings about a temporary depression of bacterial numbers, soon followed by a decided increase. Larger concentrations of CaO have a more continued depressing effect, especially above 0.5 per cent, followed by a much greater increase in bacterial development, so that, 16 weeks after the application of 0.7 per cent CaO , the numbers of bacteria rose to 420 millions per gram. Equivalent concentrations of CaCO_3 gave only very slight increases in the number of bacteria, without any depressing effect. Fischer suggested that CaO does not act merely in neutralizing the acid condition of the soil, as in the case of the carbonate, but acts in a way stimulating bacterial life. These results were confirmed by Miller who showed that the greater the amount of CaO , the more prolonged is the checking effect upon bacterial development, but the greater will be the increase in bacterial numbers when it finally sets in. Five per cent of CaO completely prevents further growth of bacteria. The CaO has, however, a selective action upon soil bacteria, since *B. fluorescens* was not stimulated by 0.1 per cent of CaO and even destroyed by 0.3 per cent; 0.1 per cent of CaO diminished nitrification of ammonium sulfate, while 0.5 per cent stopped it almost completely.

The results of the above cited investigators are in conformity with our own results. The application of CaO to the soil has a pronounced effect in disturbing or even destroying the state of microbiological equilibrium. Hutchinson (5) found that its action is intermediary between the action of antiseptics and changes induced by high temperatures and it appears to bring about a decomposition of the organic nitrogen constituents of the soil.

The fact that protozoa develop rapidly in the soil even before the maximum development of bacterial activities set in, the fact that the development of fungi is very similar to that of bacteria, the fact that the CO_2 -producing capacity of the soil is at a high level long after the protozoan development has attained a maximum, the fact that the nitrate content of the soil is depressed with the development of bacteria and fungi, then stimulated when those organisms begin to decrease,—all speak against any attempt to explain the phenomenon that has taken place by the destruction of protozoa. If there is any group of organisms that has suffered as a result of the treatment, it is the actinomycetes, which decreased from about 25 per cent of the population developing on the plate to 1–3 per cent and have not attained either their original numbers or percentage of total numbers even 150 days after treatment. This could hardly explain, however, the changes in biological activities, since in the case of some antiseptics, this depression is not so marked.

INFLUENCE OF CaCO_3

The influence of CaCO_3 upon the microbiological activities in the soil is distinctly different from that of CaO , as shown in figure 4. There was a

marked evolution of CO_2 soon after the CaCO_3 had been added to the soil, not due to biological action but as a result of chemical reactions taking place in the soil between the CaCO_3 (1 per cent) and the acid reacting substances in the soil. The rate of CO_2 production soon drops to a low level, only slightly above the control. Bacterial numbers are stimulated only to a limited extent, similar to the results obtained by Fischer (3) and Miller (9). Fungi are at first depressed, then slightly stimulated. The addition of CaCO_3 to the soil does not result in a group of phenomena characteristic of partial sterilization, since there is no decided change either in the numbers or in the interrelationships of microorganisms (equilibrium) in the soil. A bacterial

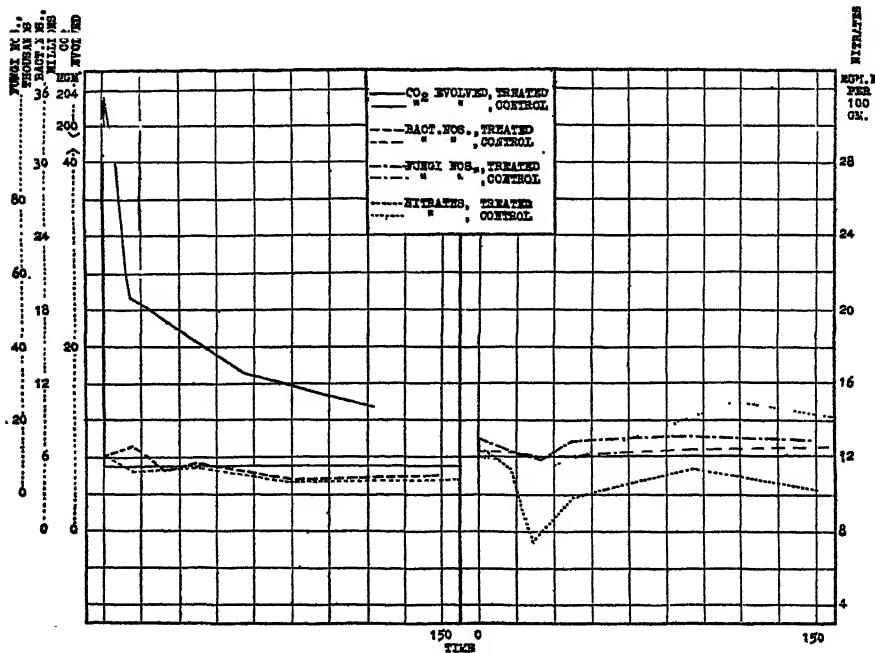


FIG. 4. INFLUENCE OF CaCO_3 ON BIOLOGICAL ACTIVITIES IN SOIL

plate from a soil treated with CaO shows a distinctly different picture from that treated with CaCO_3 . In the former the minute pin-point, slowly growing colonies predominate with some large, watery, glistening white bacterial colonies; the plate is practically free from actinomycetes colonies. The CaCO_3 treated soil shows on the plate a normal bacterial flora, with a little more stress on the typical colonies of actinomycetes.

INFLUENCE OF AIR-DRYING OF SOIL

Air-drying of the soil followed by moistening with distilled water to bring it back to optimum moisture, resulted in a decidedly stimulating effect upon

the activities of the microorganisms, as indicated by the increase in numbers of bacteria and fungi as well as CO_2 production (fig. 5). This was accompanied by a decided decrease in the amount of nitrates.

The increase in CO_2 production and diminution of nitrate content preceded somewhat the increase in numbers of microorganisms and the maximum of CO_2 production was attained before the maximum number of microorganisms. These two phenomena are probably correlated as follows: As soon as the air-dry soil is moistened, the bacteria begin to develop rapidly and the fungus spores germinate and develop into a mycelium; these activities, especially the synthesis of new cells, fungus and actinomycetes mycelium involve a rapid

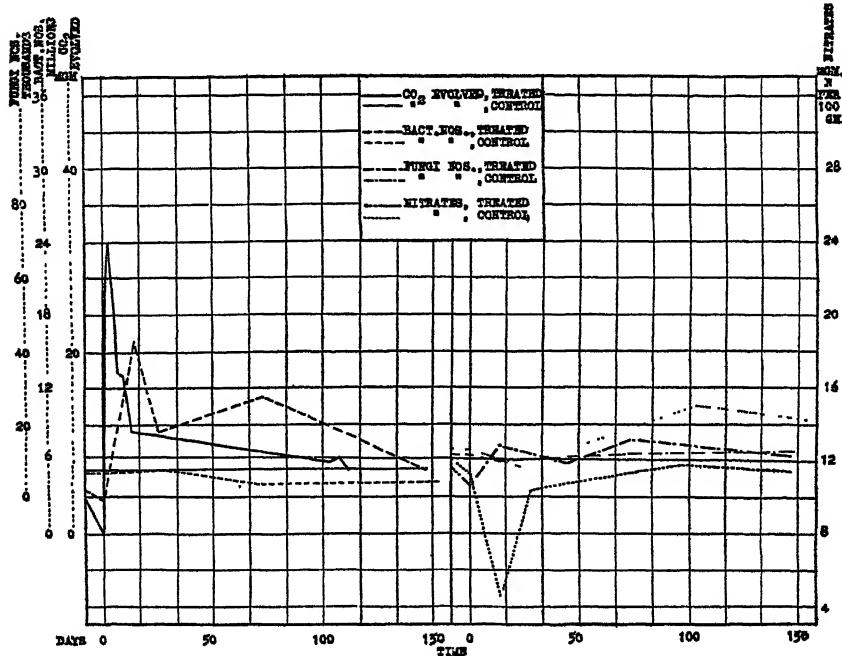


FIG. 5. INFLUENCE OF AIR-DRYING AND SUBSEQUENT REMOISTENING ON BIOLOGICAL ACTIVITIES IN SOIL

decomposition of organic matter and utilization of available nitrogen compounds (nitrates). The numbers of bacteria and fungi reach the maximum point only later, due to two influences: first, it is the development of bacteria and the maximum rate of reproduction which produce the CO_2 rather than the mere presence of the bacterial numbers as such; second, the greatest number of fungi may be indicated only after they have already completed their maximum growth, namely when they have gone into spores. Both of these phenomena will account for the fact that the maximum CO_2 production, which indicates the respiration or active growth of the organisms, precedes maximum numbers.

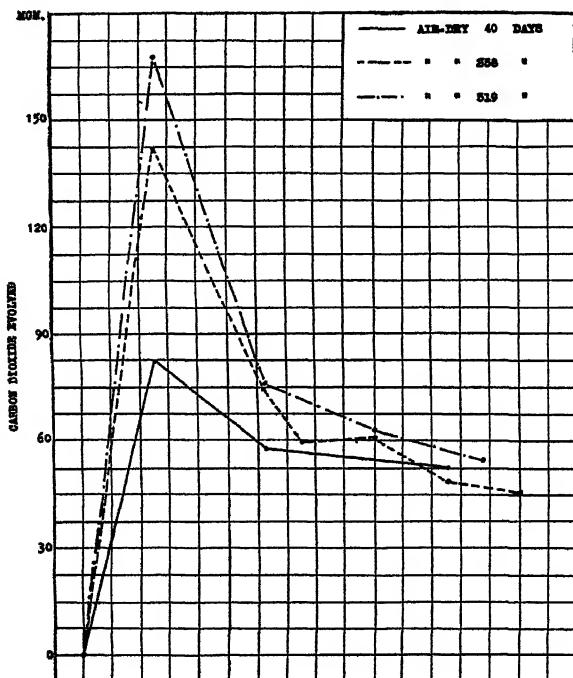
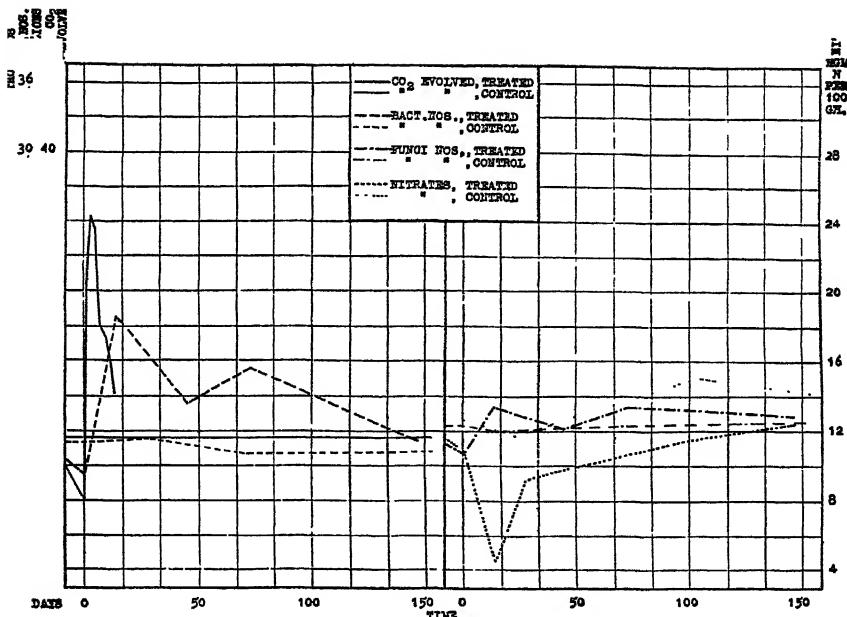
It is important to note that although air-drying of soil has a decidedly stimulating effect upon microbial activities in the soil, this effect is only of short duration: the numbers soon begin to fall off, the rate of CO₂ evolution soon reaches a maximum and the nitrate accumulation rapidly rises. Ammonia did not accumulate appreciably and, at the end of 100 days, there was only about 1 mgm. of ammonia-nitrogen in 100 gm. of soil.

The protozoa were not destroyed by the process of air-drying, the flagellates were as abundant as in the untreated soil, if not more so, while the ciliates and amoebae have disappeared temporarily; however, when the air-dry soil was inoculated with only 0.5 per cent fresh soil, the amoebae were also abundant soon after moistening. Surely the destruction of protozoa cannot account for the stimulating effect upon bacterial activities; one could just as readily, if not more so, explain the changes that have taken place by the course of growth of fungi and actinomycetes. The air-drying of the soil improved the physical condition of the soil and made organic matter more available as a source of energy to the growth of microorganisms; it also reduced the numbers of microorganisms. The bacteria and fungi were first to start growth resulting in CO₂ production and nitrate decrease; when a maximum of numbers was reached, they began to decrease. It remains to be seen whether this was due to the diminution of the available energy supply, to the development of fungi, to the increase in the proportion of actinomycetes, or to all of these combined.

The reinoculated pots gave almost exactly the same curves as the uninoculated (fig. 6); this speaks for the fact that the stimulation of bacterial activities is not due to the removal of any organisms, but merely to the change in physical condition of the soil and in the composition of the organic matter of the soil as well as to the shift of the temporary balance of the various groups of microorganisms in the soil.

The favorable influence of air-drying upon microbiological activities in the soil has also been observed by Rahn (12), Ritter (13), and others. Rahn obtained greater differences in heavy soils than in light soils, the differences were particularly marked in garden soils; this would tend to indicate that the stimulating effect of drying has to do with the modification of the organic matter in the soil; Rahn ascribed it to the degree of solubility of minerals. Ritter found that complete drying results in a greater stimulus than moderate drying; Ritter ascribed the favorable influence to a selective action upon the species of soil microorganisms. The fact that air-drying of soil brings about a decided increase in the solubility of the nutrients and change in colloidal condition of the soil has been pointed out by Kelley (7), Konig and associates (8). That air-drying of soil does not vitally affect the soil protozoa has been pointed out by Goodey and Greig-Smith.

The fact that air-drying modifies the organic matter of the soil making it a more available source of energy for microorganisms is clearly brought out in figure 7. The same soil was air-dried for 40, 358 and 519 days. At these intervals 1-kgm. portions were placed in pots, brought to optimum moisture and placed in the respirator. The longer the soil was air-dried the greater



was the maximum to which the CO₂ curve rose; the total amount of CO₂ produced from soils air-dried for different periods of time was also greater with the increase in the length of the period of drying.

INFLUENCE OF HEATING OF SOIL

Heating of soil at 65° for 1 hour resulted in somewhat different phenomena (fig. 8). Heating also produced a decrease in the number of bacteria and fungi, followed by an increase; it resulted also in a rapid increase in the amount of CO₂ formed, followed by a rapid decrease; the protozoa disappeared and did not reappear in appreciable numbers for 28 days; the content of nitrates

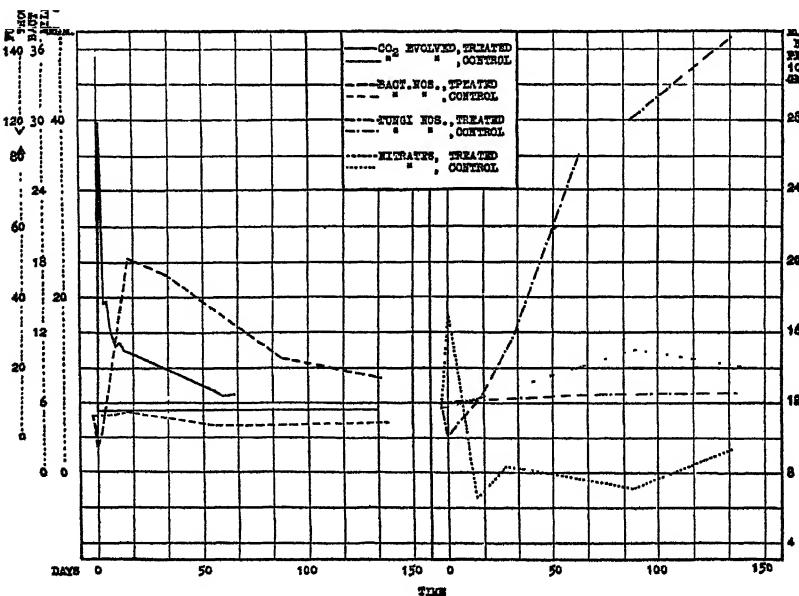


FIG. 8. INFLUENCE OF HEATING ON BIOLOGICAL ACTIVITIES IN SOIL

and other substances giving the characteristic reaction with phenol-disulfonic acid was increased as a result of heating, probably because of the complete transformation of the nitrites and possibly also of the ammonia present in the soil to nitrates; this increase in nitrate was followed by a drop accompanying the increase in the numbers of microorganisms. The bacterial numbers did not fall as rapidly as in the case of air-dried soils, but remained at a high level, even after a long period of time. However, the fungi did not increase rapidly, but only very slowly and continued to increase even after 80 days; the gradual course of increase of numbers of fungi in the soil is peculiarly parallel to the gradual fall of bacterial numbers; it is also important to note

that the nitrate content, after a slight increase, actually continued to decrease. The fact that we are not dealing here with protozoa is clearly indicated by their great abundance after 28 days treatment. Surely the large increase in numbers of fungi and soil transformations can be more readily correlated with the change in the bacterial numbers and nitrate content of soil than the presence of protozoa.

The ratio of actinomycetes to the total number of microorganisms developing on the plate was about 30 per cent before heating; this ratio dropped to about 15 per cent after heating, and about 3 per cent 2 weeks later; a gradual increase followed. In other words, the development of this group of organisms was greatly affected by heating of the soil: not only were the numbers reduced as a result of heating, but they did not increase until considerable time elapsed and even 4 months after treatment their ratio to the total number was only one-fourth of that before the treatment of the soil. The two phenomena, the rapid development of fungi and the slow, delayed growth of the actinomycetes as a result of soil treatment are fully correlated with the increase of bacterial numbers followed by a slow gradual decrease. It may be of interest to record that 57 days after the last determination reported in the curves the bacteria were on about the same level, the fungi began to decrease, while the nitrates nearly approached that of the control.

When the heated soil was reinoculated with 0.5 per cent of fresh soil (fig. 9), the protozoa began to develop much more rapidly, appearing abundantly after 14 days. The curve for CO_2 production was similar to the curve in uninoculated soil. The bacterial numbers reached a higher maximum, but began to drop much more rapidly; however, after 85 days they were on the same level with the uninoculated soil. The numbers of fungi behaved contrary to expectation, and contrary to the experiments reported in the previous paper; they remained consistently low for a long time and only 4½ months after treatment did they show the marked increase which was observed in the other treated soils. This delayed development may be due to improper inoculation (only 0.5 per cent of soil used), to the destruction of the fungi capable of developing in the heated soil, or to the difference in the mycelial and spore development of the particular organisms. The nitrates decreased parallel with the increase of bacteria and began to increase with the drop in bacterial numbers. There was a much more rapid development of the nitrate content in the inoculated than in the uninoculated soil, due to the slow development of the fungi and the reintroduction of the nitrifying organisms. After 4 months, however, the nitrate accumulation is as rapid in the uninoculated as the inoculated soil. This may be due to the rapid development of the fungi which corresponds to a slowing down of the increase in nitrate accumulation as found in the uninoculated soil. The ratio of actinomycetes in the inoculated soil is similar to the ratio in the uninoculated. Two months after the last point on the curve, the fungi were found to be rapidly diminishing in numbers and the nitrate increasing. There was no appreciable increase

in the amount of ammonia in both heated soils, since the determination for ammonia was made several months after treatment (because of the scarcity of the soil) when the nitrifying bacteria became again active.

Steaming soils brings about a greater solubility of organic soil constituents, as pointed out by Richter [see Fischer (3)], Pickering (11), Elveden (2) and others. Fischer also observed a decided drop of the rate of CO_2 production following a rapid rise in inoculated steamed soils, while the bacteria remained at a high level. He explained this by the fact that, after a period of decided activities, the bacteria become more or less inactive, going

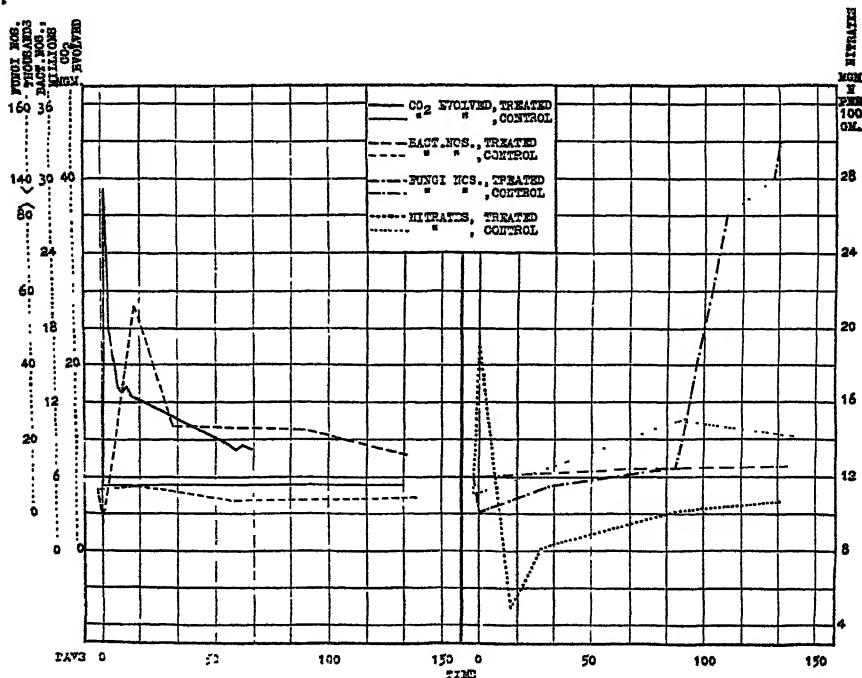


FIG. 9. INFLUENCE OF HEATING AND REINOCULATION ON BIOLOGICAL ACTIVITIES IN SOIL

into resting stages, which possess only a low respiratory power, but which are capable of developing into colonies on the plate. The stimulating effect upon bacterial activities was considered to be due to the decomposition of the bacterial bodies. Greig-Smith (4) suggested that the effect of heat upon soil is to destroy the bacterial toxins present there. Russell and Hutchinson explained it by the destruction of protozoa, although, as the figures show, the fungi curves have the same tendency as the bacteria curves, especially in reinoculated soils. Bolley (1) suggested that the destruction of disease-producing fungi and bacteria in the soil by heat has more to do with the increase in soil productiveness than any other phenomenon. Jachshevski (6) ascribed the cause of soil fatigue to fungi. The results in these experiments bear out the fact that fungi are destroyed by heat treatment; then those that survive (some typical soil fungi) reproduce rapidly to great abundance.

INFLUENCE OF TOLUENE TREATMENT

Treatment of soil with toluene (fig. 10) brought about an increase in the rate of CO₂ production, followed by rapid decrease; this was accompanied by a decided increase in bacterial numbers; this increase remained at a high level for a long time before any appreciable decrease was observed and, even after 130 days, the numbers were still almost twice as high as in the untreated soil. The fungi were practically destroyed as a result of the treatment of the soil with the disinfectant and began to increase only slowly, then more rapidly; when they reached their highest point the fungi and the bacteria began to decrease, both remaining however at a much higher level than the control. Actinomycetes were only about 10 per cent of the flora developing on the plate instead of the 30 per cent in the control. The protozoa at first disappeared, then reappeared after 28 days. The nitrates were greatly diminished during and soon after treatment, but, after a prolonged period of time, they began to increase. No rapid multiplication of actinomycetes and fungi took place in this soil as was found in the case of a soil rich in organic matter (5A).

When the toluene-treated soil was inoculated with fresh soil, the rate of CO₂ production as well as the bacterial numbers rose above the uninoculated soil, but the bacterial numbers dropped down also more rapidly (fig. 11). The fungi did not reach such a high point as in the uninoculated soil, but after 130 days both soils had about the same number of fungi. The actinomycetes ratio was about the same as in the uninoculated soil. The protozoa were abundant even after 14 days. The nitrates were also diminished rapidly during and soon after toluene treatment, but they began to increase sooner than in the uninoculated soil.

Several points need be emphasized here:

1. An increase in bacterial numbers is always sooner or later followed by a decrease. May it not be possible that, since in the reinoculated soil the maximum goes up higher than in the uninoculated, the drop is also sooner?
2. The increase in the number of fungi does not seem to depend primarily on the forms introduced but upon the capacity of the treated soil to support a fungus population. Among the fungi surviving toluene treatment we find most noticeable the genera *Zygorhynchus*, soil *Penicillium* (pink-yellow form) *Cunninghamella* and *Cephalosporium*, all typical soil forms.
3. The nitrate bacteria are not completely destroyed by the treatment with toluene, they are only temporarily suppressed in the uninoculated soil, since they become always active again, sooner, of course, in the reinoculated soil.
4. Although all previous work noted (Russell and Hutchinson etc.), as well as our own results reported in the first part of this paper, indicate that toluene treatment of soil leads to an accumulation of ammonia, we did not find any increase in this particular case. This may be due to one or more causes' (a) The ammonia was determined only after 120 days, since we did not want to remove from the pots any large quantities of soil which would be necessary for ammonia determinations, and at that time all the ammonia might have already been converted into nitrates. (b) In this particular instance the soil was rich in nitrates before treatment with the disinfectant; it is therefore possible that in this case the soil bacteria

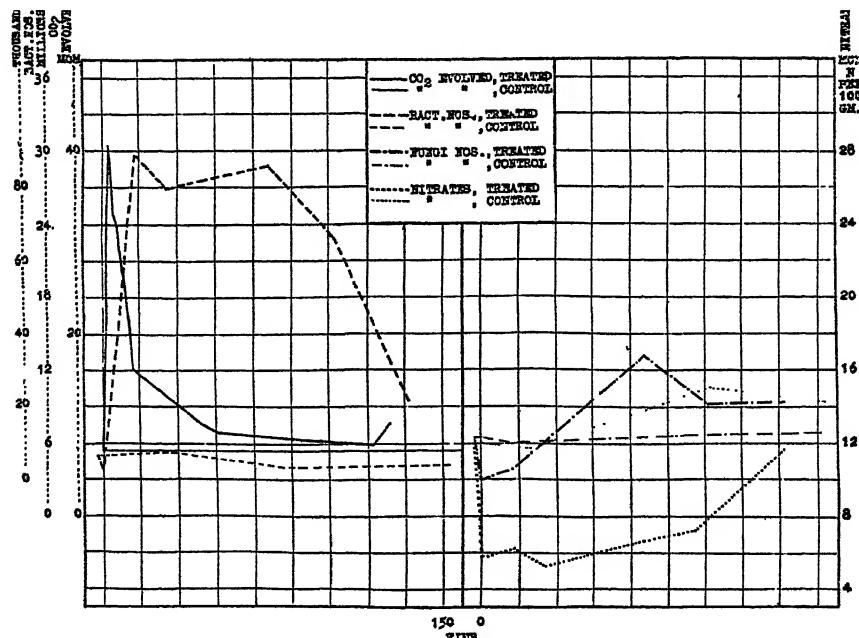


FIG. 10. INFLUENCE OF TOLUENE ON BIOLOGICAL ACTIVITIES IN SOIL.

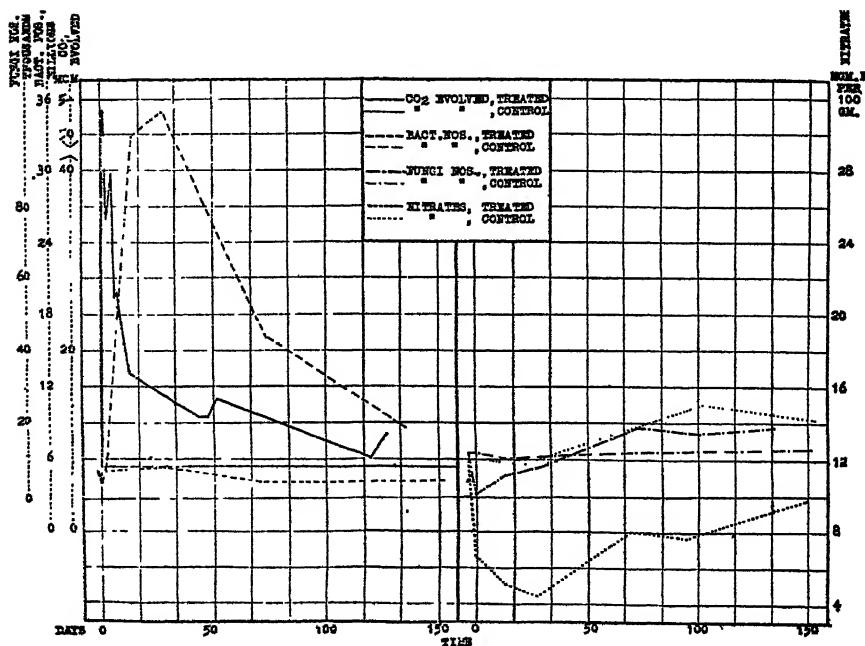


FIG. 11. INFLUENCE OF TOLUENE AND REINOCULATION ON BIOLOGICAL ACTIVITIES IN SOIL.

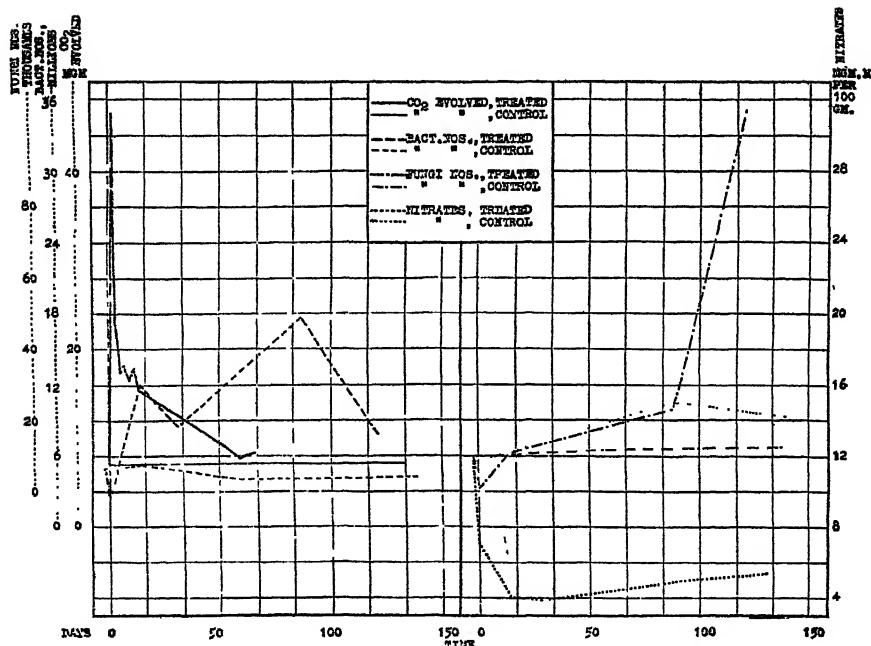
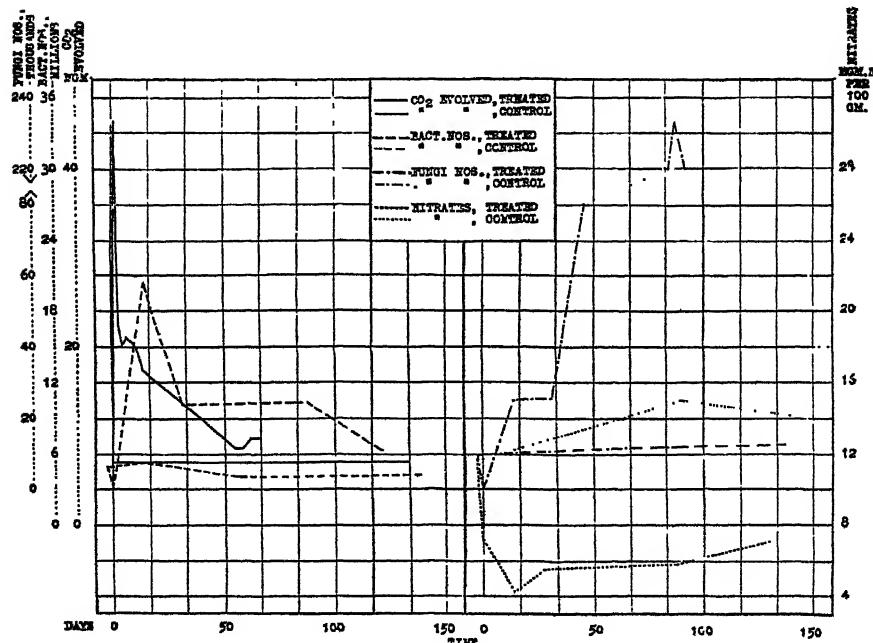
and fungi did not break down readily the soil proteins and other nitrogenous compounds, but used the various carbon compounds (of a non-nitrogenous nature) as sources of energy using up the nitrate as a source of nitrogen and not liberating any ammonia. (c) It is also possible that in the period of 11 months that the soil was kept under favorable moisture and temperature conditions, all the readily decomposable nitrogen compounds were decomposed and the nitrogen finally converted into nitrate; the treatment with toluene therefore could not result in rendering a soil, which was not very rich in organic matter, containing no nematodes, worms and insects, and only comparatively small numbers of fungi, richer in available nitrogenous compounds.

INFLUENCE OF CARBON BISULFIDE

Treatment of soil with 1 per cent of carbon bisulfide (fig. 12) resulted in phenomena very similar to the toluene treatment, heating of soil, air-drying, CaO treatment; the curves are, however, not only not identical but in some cases distinctly different, depending on the interrelationships of the various groups of organisms. The CO₂ production curve is quite similar to the other curves; protozoa were absent after 14 days and began to appear only after 28 days. Bacteria were at first depressed, then began to increase rapidly, reaching a maximum only after 90 days. The percentage content of actinomycetes was again reduced to a minimum and even after 120 days did not reach more than $\frac{1}{3}$ of the original proportion. The fungi were also depressed and soon recovered, but only very slowly; it is important to note that the rapid rise of numbers of fungi coincides almost exactly with the precipitous drop of bacterial numbers. The nitrate content in the soil was appreciably reduced as a result of treatment and soon after; in view of the fact that the nitrifying bacteria were put out of action, even if temporarily, there was no appreciable further increase in nitrate even after 120 days; the ammonia content, however, increased appreciably from less than 1 mgm. to over 3 mgm. per 100 gm. of soil.

In the case of the reinoculated soils (fig. 13), the same curve of CO₂ production is obtained with a more rapid rise in bacterial numbers. The rapid rise was also followed by a rapid fall. The protozoa were already evident after 14 days. These could hardly explain the precipitous fall of bacterial numbers, witness the almost coincident rise of fungous numbers. The fungi recovered in the reinoculated soil much more rapidly and began to rise precipitously after 35-40 days, this corresponding to the rapid drop in bacteria. The nitrate was here also reduced, but began to increase somewhat earlier than in the uninoculated soils, the gain was made partly at the expense of the ammonia in the soil. Determinations made 70 days after the last points on the curve indicated a drop in the numbers of fungi accompanied by a rise in the nitrate content of the soil.

The stimulating effect of disinfectants, especially carbon bisulfide upon the decomposition of organic matter in the soil has been pointed out previously by various investigators, using, as an index of the decomposition of organic matter, carbon dioxide production, oxygen absorption, and ammonia accumu-

FIG. 12. INFLUENCE OF CS₂ ON BIOLOGICAL ACTIVITIES IN SOILFIG. 13. INFLUENCE OF CS₂ AND REINOCULATION ON BIOLOGICAL ACTIVITIES IN SOIL

lation. While some ascribed this to the direct stimulating action of the disinfectant upon biological activities, others to the neutralization of soil toxins, modification of organic matter, change in physical condition of soil, Russell and Hutchinson ascribed it to the destruction of protozoa and Hiltner and Störmer to the destruction of the bacterial equilibrium in soil. According to the latter investigators, the disinfectant opens a way for an entirely new bacterial development, achieved by the unequal retardation and stimulation in the growth of the different groups of microorganisms; some become disproportionately prominent and others are almost entirely suppressed.

Stoklasa (14) suggested that the stimulating effect of the disinfectant is due to the destruction of a definite number of soil microorganisms; the surviving bacteria readily break down the dead organisms, liberating phosphate and other ions, which now become available for plant growth.

The following two curves, having nothing to do with disinfectants (although sulfur is looked upon as such by certain investigators) show the influence of available organic matter and of a small amount of sulfur upon the soil microbiological activities.

The addition of 0.2 per cent of ground dry alfalfa meal (2 gm. per 1 kgm. of soil) resulted in changes in the microbiological activities very similar to partial sterilization of soil (fig. 14). The curve for CO_2 production rose immediately, then fell precipitously. The rise in bacterial numbers followed soon after the rise in the CO_2 curve exactly as in the case of partial sterilization; the numbers remained at a rather high level for a long time, then decreased rapidly. The fungi rose rapidly, then began to diminish only slowly. The nitrates dropped rapidly, then began to increase. The curves in general are quite similar to the curves of steamed or toluene-treated soils that were reinoculated. The protozoa, of course, were not injured as a result of addition of readily available organic matter. This seems to suggest that the stimulating influence of heat and treatment with volatile antiseptics, outside of the destruction of fungi and other pests causing plant diseases, may be due to an increase in the available plant food in the soil either as a result of modification of the organic matter in the soil or destruction of various worms, protozoa, fungi, etc.

The addition of a small amount of sulfur (500 mgm.) to 1 kgm. of soil resulted (fig. 15) in a slight decrease in the numbers of bacteria, slight increase in the number of fungi and slight increase in the CO_2 -producing capacity of the soil. The original decrease in nitrate content cannot be explained other than by the variability of the nitrate content in the particular soils. Fifty-four days after the last point on the curve was drawn, the sulfur-treated soils were again analyzed showing a steady decrease in the number of bacteria and increase in the number of fungi, the former dropping to 2,900,000 per gram and the latter going up to 25,000 per gram. The increase in soil acidity made the soil a poorer medium for the growth of bacteria and a better medium for the growth of fungi.

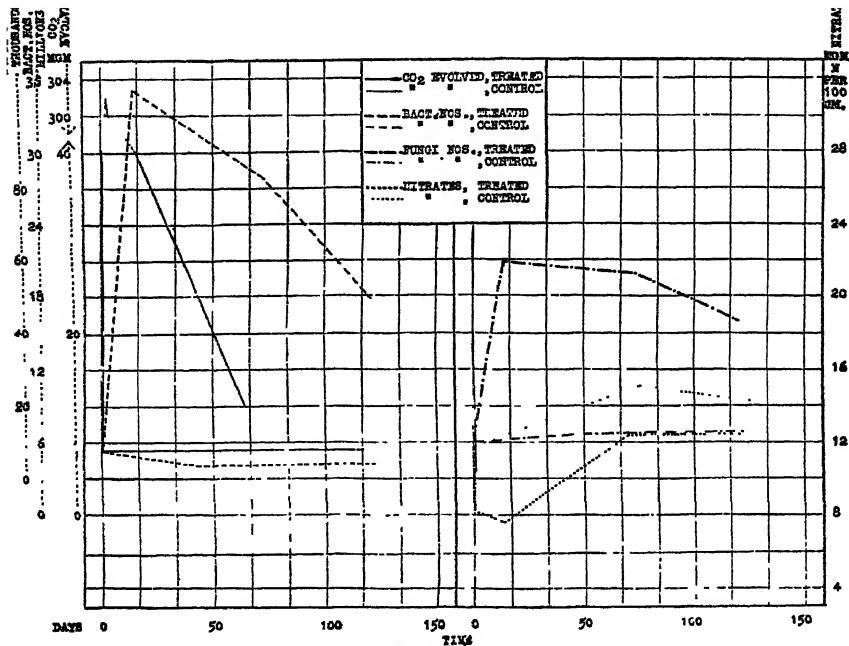


FIG. 14. INFLUENCE OF ORGANIC MATTER ON BIOLOGICAL ACTIVITIES IN SOIL

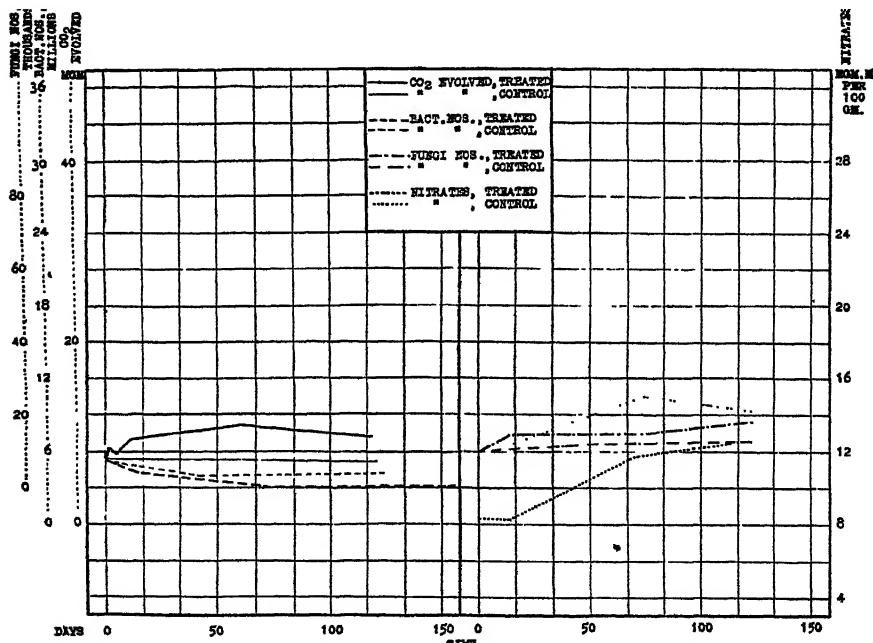


FIG. 15. INFLUENCE OF SULFUR ON BIOLOGICAL ACTIVITIES IN SOIL

The soils treated with K_2SO_4 and $CaHPO_4$ and these salts plus $NaNO_3$ did not show any different results from the ordinary cultivated (tilled) soils, so that they are not included here. This is probably due to the fact that the soils in question, due to their long incubation period, contained sufficient soluble minerals and nitrogen compounds, so that these did not become limiting factors.

Figure 16 indicates the total amounts of CO_2 given off by the soils the first week after treatment. The CaO treated soils are not included here since they gave off no CO_2 the first week. However, if the total CO_2 given off by the variously treated soils could have been determined, the CaO treated soils would have given as high results as any in the series, with the exception

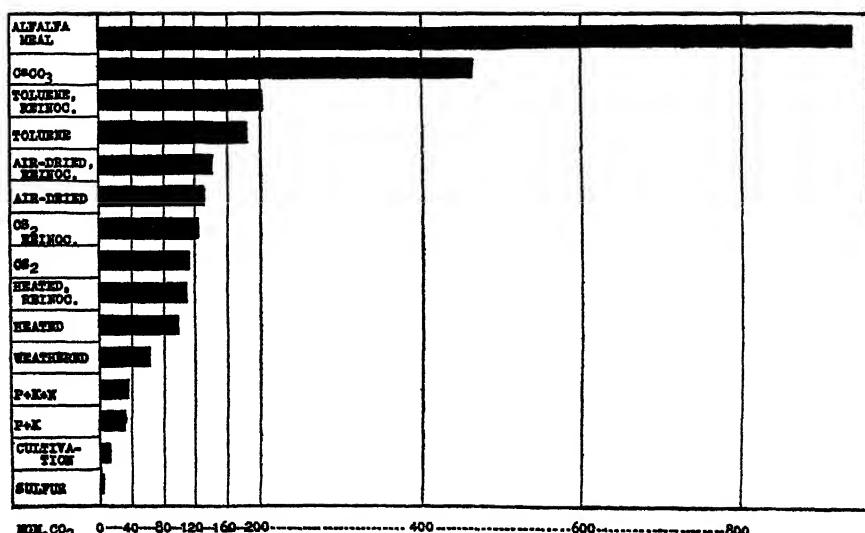


FIG. 16. CARBON-DIOXIDE PRODUCTION EFFECTED BY VARIOUS TREATMENTS—TOTAL CO_2 PRODUCED DURING FIRST WEEK AFTER TREATMENT

of the alfalfa treated soils. This is realized from the fact that the CO_2 remained at a high level in the CaO treated soils longer than in the case of any other treatment.

SUMMARY

A soil with a known history as far as microorganisms and their activities are concerned has been prepared. The results of the influence of partial sterilization of soil by volatile antiseptics, heat, and CaO upon the numbers of bacteria, fungi, actinomycetes, protozoa and their activities in the soil thus prepared are reported. These are compared with the influence of air-drying, addition of $CaCO_3$, small amounts of organic matter and sulfur upon the same microbiological activities.

REFERENCES

- (1) BOLLEY, H. L. 1910-1913 Interpretation of results in experiments upon cereal cropping methods after soil sterilization. *In* Science, v. 33, p. 229-234; v. 32, 529-541; v. 38, p. 48-50, 249-259; N. D. Agr. Exp. Sta. Bul. 107.
- (2) ELVEDEN, V. 1921 A contribution to the investigation into the results of partial sterilization of soil by heat. *In* Jour. Agr. Sci., v. 11, p. 197-210.
- (3) FISCHER, H. 1909 Versuche über Bakterienwachstum in sterilisiertem Boden. *In* Centrbl. Bakt. (etc.), Abt 2, v. 22, 671-675.
- (4) GREIG-SMITH, R. 1911 The bacteriotoxin and the agricere of soils. *In* Centbl. Bakt. (etc.), Abt 2, v. 30, p. 552.
- (5) HUTCHINSON, H. B. 1913 The partial sterilization of the soil by means of caustic lime. *In* Jour. Agr. Sci., v. 5, p. 320-330.
- (6) JACHSHEVSKI, A. 1912 On the causes which determine infertility of the soil and loss of crops. *In* Khosiaistvo (Kiev), v. 7, no. 34, p. 1103-1108; *cited in* Inter. Inst. Agr. Bul. Agr. Intel. Pl. Dis., v. 3, p. 2528-2531.
- (7) KELLEV, W. P. 1915 Ammonification and nitrification in Hawaiian soils. Hawaii Agr. Exp. Sta. Bul. 37.
- (8) KONIG, J., HASENBÄUMER, J., AND GLENK, K. 1913 Über die Anwendung der Dialyse und die Bestimmung der Oxydationskraft für die Beurteilung des Bodens. *In* Landw. Vers. Sta., v. 79-80, p. 491-534.
- (9) MILLER, F. 1914 Über den Einfluss des Kalkes auf die Bodenbakterien. *In* Ztschr. Gärungsphysiol., v. 4, p. 194-206.
- (10) MIYAKE, K. 1916 On the nature of ammonification and nitrification. *In* Soil Sci., v. 2, p. 481-492.
- (11) PICKERING, S. U. 1910 The activities of heat and antiseptics on soils. *In* Jour. Agr. Sci., v. 3, p. 32-54, 258-276, 277.
- (12) RAHN, O. 1908 Bakteriologische Untersuchung über das Trocknen des Bodens. *In* Centrbl. Bakt. (etc.), Abt. 2, v. 20, p. 38-61.
- (13) RITTER, G. 1912-1913 Das Trocknen der Erden. *In* Centbl. Bakt. (etc.), Abt. 2, v. 31, p. 116-143, v. 36, 346.
- (14) STOKLASA, J. 1911 Biochemischer Kreislauf des Phosphat-Ions im Boden. *In* Centbl. Bakt. (etc.), Abt. 2, v. 29, p. 185.
- (15) WAKSMAN, S. A. 1923 Microbiological analysis of soil as an index of soil fertility. IV. *In* Soil Sci., v. 15, p. 49-65.
- (16) WAKSMAN, S. A., AND STARKEY, R. L. 1923 Partial sterilization of soil, microbiological activities and soil fertility. I. *In* Soil Sci., v. 15, p. 137-158.

THE CHLOROSIS OF PINEAPPLE PLANTS GROWN ON MANGANIFEROUS SOILS

W. T. McGEORGE

Experiment Station Hawaiian Sugar Planters' Association

Received for publication July 1, 1923

Plants which do not make normal growth often develop a chlorotic condition of the leaves usually attributed to certain nutritional disturbances. Such a condition is more often noted on calcareous soils although other factors have been cited. The chlorosis of pineapple leaves on plants grown on the manganese soils of Hawaii is an example.

In an investigation of these manganese areas and the nutritional disturbances of numerous plants grown on these soil types Kelley (9) has reached the following conclusions. "From these evidences we may believe that the effects of manganese are largely indirect and are to be explained on the basis of its bringing about a modification in the osmotic absorption of lime and magnesia, and that the toxic effects are chiefly brought about through this modification rather than a direct effect of the manganese itself. . . . The percent of lime is increased while the absorption of magnesium and phosphoric acid is decreased. . . . in practically every instance a modification of the mineral balance was observed and this was found to follow the same direction. . . . regardless of whether the plant showed a toxic effect.

Gile (3) has noted a development of chlorosis on pineapple plants grown on calcareous soils in Porto Rico. He found the application of iron salts to the leaves to be very effective and to induce normal growth.

Johnson (8) on the basis of Gile's work applied solutions of iron salts to the leaves of pineapple plants suffering from chlorosis on the manganese areas in Hawaii and noted a return of the plant to normal growth. While he appears to have published no record of laboratory investigations he concluded that the chlorosis was due to a locking up of the iron by the manganese in an unavailable form in the soil. By a recalculation of a selected part of Kelley's data he then proceeded to substantiate his interpretation by showing a lower iron content in those plants which had become chlorotic. A study of Kelley's data *in toto* (9) does not indicate such to be true. The iron content of the ash of all plants analyzed shows considerable variation but no consistant relation to the manganese content of the soil. This is especially true of the pineapple plant of which Kelley made four analyses and of which only one, that cited by Johnson, showed an appreciably lower iron content in the plant grown on manganese soil as compared to that grown on a normal soil.

In a recent study on the nature of acidity in Hawaiian soils the writer has noted certain peculiarities which may throw some light on the chlorosis of pineapple leaves grown on these manganese areas. Hawaiian soils are usually acid in reaction although they are characteristically basic, that is very high in iron, aluminum and manganese oxides which are often in excess of silica. The iron content of these soils, expressed as Fe_2O_3 , varies greatly and usually falls within the range of 20-30 per cent. This is true of the manganese areas as well as other types.

In a study of the relative acidity in manganiferous and non-manganiferous types, samples of soil and subsoil were taken representing both types. The acidity expressed as pH is given in table 1.

The manganese content of the nonmanganiferous samples was not determined but soils from the locality usually contain less than .5 per cent Mn_3O_4 . The characteristic color of the manganese type is a chocolate brown changing to a red subsoil at 8-12 inches. The lower manganese content of the subsoil is typical. The subsoil samples represent the depth below change of color to two feet. With change of color there is also a notable change in physical texture. The top soil contains a higher silt and fine sand content and may be classed as a silty loam while the subsoil merges into a clay loam. This may be attributed to the deposition of manganese upon the soil grains thereby increasing their size. It is typical of the manganese type that the manganese is present as MnO_2 in the form of concretions or deposited as a film on the surface of the soil grains.

TABLE 1
Showing acidity of two soil types expressed as pH

NATURE OF SOIL	SURFACE SOIL		SUBSOIL	
	Mn_3O_4 content	Reaction	Mn_3O_4 content	Reaction
Manganiferous.....	per cent	pH	per cent	pH
	7.3	5.9	3.5	6.5
	4.5	5.9	3.0	6.7
Nonmanganiferous.....	4.7	6.0	3.9	6.7
		6.6		6.5
		5.9		6.1
		4.5		4.3

The interaction between metallic elements in solution is governed, theoretically at least, by their relative positions in the electromotive series, each element replacing another standing lower in the series until a certain equilibrium is reached. The relative position of the more important elements present in the soil is as follows; potassium, sodium, calcium, magnesium, aluminum, manganese, iron. It must be admitted however that in a soil other factors such as hydrolytic action, basic replacement and double decomposition must be considered. Yet it is evident from the above that iron standing lowest in the series should be present in less concentration in the soil solution and that calcium and aluminum should exercise a greater displacing action than manganese, being higher in the series, and should further displace manganese itself.

In studying the relative solubility of iron and manganese in these acid soils it was found that iron salts were present in highest concentration in those soils of pH 5.5 or lower. That manganese is a factor principally in

those soils of pH 5.5 or higher. This applies to all types regardless of the actual manganese present in the soil. That is whether high or low.

Now with commercially grown crops here in the islands those which appear to produce normal growth on highly calcareous soils also grow with least disturbance on the manganiferous types. Reference is made to sugar cane and sisal (*Agave Sisalana*), more particularly the latter. Up until a recent date there were two sisal plantations on the island of Oahu. One was located in the coral areas practically devoid of soil and the other in the heart of the manganiferous areas. Plants grew normally in both but slightly better on the manganese soil due to better environment. Johnson has noted (8) that the calciphilous legumes are among the most strongly affected on manganese soils and claims that manganese is the cause of the chlorotic condition. He fails to point out however that *Crotalaria*, one of the most widely distributed legumes in the islands, grows luxuriantly on the manganese soils (9). This seems more tenable from Truog's work (10) in which he found all degrees of lime requirement in legumes as well as non-legumes.

Gile (3) found that it was possible to obtain a normal growth of pineapples on a soil containing approximately 30 per cent lime by heavy fertilization with stable manure. Kelley (9) found the same to be true on the manganese soils. The manganese present in Hawaiian soils is extremely soluble in organic acids. It hardly seems tenable that the fertility of these soils would be increased by heavy applications of organic fertilizers if the toxicity is due directly to manganese.

In studying the relation of iron, aluminum, manganese and lime to soil acidity in Hawaiian soils it was found that as compared to aluminum both iron and manganese appear to be only a small factor in determining the reaction. The aluminum content of these soils is approximately equal to that of iron but in measuring the solubility in dilute mineral acids and other weak solvents aluminum is dissolved in considerable excess. This also is in agreement with the respective position of these elements in the electromotive series. Also there is a direct relation between the solubility of lime and acidity. Table 2 shows the relation between the per cent of lime soluble in water saturated with CO₂ (shaking 1 part soil to 5 parts water) and the soil reaction.

Table 2 might be taken to indicate that lime is closely related to the concentration of the elements iron, aluminum and manganese in the soil solution of Hawaiian soils. Kelley (9) claimed that these manganese areas are of alluvial origin, that the manganese has been brought into solution by leaching and ultimately deposited in the low lying pockets. This theory is born out by the sporadic occurrence of the manganese spots which are usually lower than the surrounding non-manganiferous types. Judging from their respective positions in the electromotive series it is evident that the lime present in the soil solution is the principle factor in this deposition of manganese. It is usually present in excess of all other elements in the

soil solution and water extracts of Hawaiian soils. This further explains the lower hydrogen-ion concentration in the subsoils of manganeseous types. By replacement of manganese the concentration of calcium in the soil solution is increased. Because of the loose texture of this soil type this solution passes easily from the top soil into the subsoil. The humus content of these soils is very low. The hydrogen-ion concentration appears to be due principally to the presence of acid-reacting silicates. The lime is fixed in the subsoil by these acid aluminum silicates forming silicates of lesser acid tendencies. On determining the solubility of lime in CO_2 -saturated water the results shown in table 3 were obtained with the three manganese soils and subsoils.

These results appear to indicate the presence of silicates of lesser acid tendencies in the subsoil. It will be noted that the solubility in the subsoil is lower than the soil yet the hydrogen ion concentration is lower. The

TABLE 2
Relation of lime to pH values of typical Hawaiian soils

Soil No.....	848	367	399	765	186	621	722	872	3
Per cent of CaO ...	0.008	0.009	0.013	0.015	0.017	0.023	0.033	0.081	0.131
pH values.....	4.63	4.88	4.97	5.66	5.73	5.98	7.00	7.67	8.01

TABLE 3
Relation of solubility of CaO in soil and subsoil

	SOIL 1		SOIL 2		SOIL 3	
	Top soil	Subsoil	Top soil	Subsoil	Top soil	Subsoil
Per cent of CaO.....	0.023	0.017	0.015	0.010	0.028	0.022
pH values.....	5.9	6.5	5.6	6.7	6.0	6.7

higher solubility of lime in the manganese soils as compared to the normal red soil is typical. This greater solubility of lime, the activity toward the replacement by calcium of manganese, aluminum and iron in solution, the open texture and good aeration in such types which assures a ready supply of air and carbon dioxide for the solution of calcium as bicarbonate appear to be important factors in the chlorosis of pineapple plants grown on this soil type. It might also be mentioned at this point that pineapple roots are almost entirely confined to the surface soil. Also that the development of chlorosis usually follows liming even on the more acid island soils.

Wilcox and Kelley (11) in an anatomical examination of the physiological disturbances in plants grown on manganese soils noted a superabundance of calcium oxalate crystals in the chlorotic pineapple leaves. The chemical analysis of leaves has also shown a markedly higher lime content as compared to the normal green leaves.

AVAILABILITY OF IRON

Comber (2) has developed a qualitative test for soil acidity in which he shakes the soil with a solution of KSCN in alcohol. By increasing the concentration of $\text{Fe}(\text{SCN})_3$ in the liquid phase by the use of this solvent he obtains a very delicate test for iron indicating the presence of acid reacting salts of this element and aluminum. The delicacy of this test is further increased by using an ether-alcohol solvent for the reagent. As thus applied to the manganese soils all showed a positive test for iron in solution. The depth of color is just as great as in the nonmanganiferous soils of equal hydrogen-ion concentration. One difference was noted however. The color of the test gradually fades in those soils of pH 6.0 or higher to a greenish blue. This is due to the presence of manganese as dioxide and not to the presence of manganese salts in solution. This was noted in the normal soils containing as low as .4 per cent MnO_2 and was produced in a soil of pH 4.3 by the addition of MnO_2 but not by the addition of any amount of manganese salts.

Comber (2) attributes this reaction to a double decomposition while Carr (1) suggests the actual solution of iron and aluminum which existed previously as colloidal basic salts. In either case the test indicates the presence of iron in readily available form in the manganiferous type and that MnO_2 does not hold the iron in an unavailable combination.

MOBILITY OF IRON

In a very thorough study of the availability of iron and its mobility in the plant, Gile and Carrero (4, 5, 6, 7) have shown certain factors to greatly influence the mobility of iron in the leaves. They found that chlorotic leaves on calcareous soils when restored to normal color by spraying with iron salts do not transfer this iron to new leaves but the new leaves must be sprayed in order to maintain the green color of the plant as a whole. That is to say, with the withering of the old leaves the iron is not transported to the new. In the commercial spraying of pineapple plants of Hawaii which is successfully practised on an extensive economic scale, plants grown on all soils show a response to spraying with solutions of ferrous sulfate. Of course, this is most marked on the manganese soils where the chlorotic condition is more prevalent. Also the spraying must be continued at intervals throughout the life of the plant. These facts clearly indicate the low mobility of iron even in the normal pineapple plants.

CONCLUSIONS

It is believed that the forgoing results indicate that the chlorosis of pineapple leaves on plants grown on manganese soils is due to a greater assimilation of lime indirectly caused by the presence of manganese in excessive amounts in the soil.

That the principal physiological disturbance is the greater immobility of iron in the plant resulting from the excessive lime content of the leaves and stalk and the low rate of mobility of iron even in normal pineapple leaves.

Iron is shown to be present in equally available form in both manganiferous and nonmanganiferous soil types of equal hydrogen-ion concentration. The fact that the addition of soluble iron salts to the soil is without effect and that new leaves must be sprayed indicates lack of mobility in the plant to be the principle inhibiting factor.

It is not denied that manganese under certain conditions may exert a toxic effect on plants. Numerous references in literature tell of such. This is especially true in water and sand cultures carried on in the absence of the complexities of soil environment. Also it is recognized that manganese may displace iron in solution in water and sand cultures. The relative positions in the electromotive series proves this, but it also indicates that lime functions as such with relatively greater activity.

REFERENCES

- (1) CARR, R. H. 1921 Measuring soil toxicity, acidity and basicity. *In* Jour. Indus. and Engin. Chem. v. 13, p. 931-933.
- (2) COMBER, NORMAN M. 1920 A qualitative test for sour soils. *In* Jour. Agr. Sci., v. 10, p. 420-422.
- (3) GILE, P. L. 1911 Relation of calcareous soils to pineapple chlorosis. Porto Rico Agr. Exp. Sta. Bul. 11.
- (4) GILE, P. L., and CARRERO, J. O. 1914 Assimilation of colloidal iron by rice. *In* Jour. Agr. Res., v. 3, p. 205-210.
- (5) GILE, P. L., and CARRERO, J. O. 1916 Immobility of iron in the plant. *In* Jour. Agr. Res., v. 7, p. 83-87.
- (6) GILE, P. L., and CARRERO, J. O. 1916 Assimilation of iron by rice from certain nutrient solutions. *In* Jour. Agr. Res., v. 7, p. 503-528.
- (7) GILE, P. L., and CARRERO, J. O. 1917 Absorption of nutrients as affected by the number of roots supplies with the nutrient. *In* Jour. Agr. Res. v. 9, p. 73-95.
- (8) JOHNSON, MAXWELL, O. 1917 Manganese as a cause of the depression of the assimilation of iron by pineapple plants. *In* Jour. Indus. and Engin. Chem., v. 9, p. 47-49.
- (9) KELLEY, W. P. 1912 The function and distribution of manganese in plants and soils. Hawaii Agr. Exp. Sta. Bul. 26.
- (10) TRUOG, EMIL. 1918 Soil acidity: I. Its relation to the growth of plants. *In* Soil Sci. v. 5, p. 169-195.
- (11) WILCOX, E. V. and KELLEY, W. P. 1912 The effect of manganese on pineapple plants and the ripening of the pineapple fruit. Hawaii Agr. Exp. Sta. Bul. 28.

THE EFFECT OF MOISTURE ON SOIL COLOR

A. M. O'NEAL¹

Iowa Agricultural Experiment Station

Received for publication July 1, 1923

The color of soils is one of the most important characteristics upon which their classification depends. But soil colors are not readily determined. There are no definite standards which may be utilized as a basis for comparison when soils are mapped.

In an earlier publication (1) attention was called to the difficulties which soil surveyors encounter in the field, when they are mapping, because of color variations in soils and uncertainty regarding the exact meaning of the terms used in color descriptions. It was shown in a study of several soil types, that descriptions of soil colors, as given by different men, vary considerably, particularly when light colored soils are described. The personal equation seems to play an important part in the descriptions. But there are other factors involved. The lack of a definite terminology for soil colors causes a groping for the right descriptive terms and hence long uncertain descriptions are often given especially for light colored types. Then too, the seasonal conditions seems to play a part for the same man may describe the same type somewhat differently in a different season. Hence the question is raised whether descriptions of soil colors should be based on air-dry samples or on field observations.

The official descriptions of soil series as given by the Bureau of Soil are based on air-dry samples but the soil survey reports give the color descriptions devised by the field men from their actual observations in the field. In other words the surveyors map and describe soils as they find them in the field, that is, with varying amounts of moisture, depending on the seasonal conditions. In future work it seems probable that the same practice will be continued owing to the impossibility of mapping soils on an air-dry basis.

It is obvious, then, that one of the first steps necessary in the solution of the problem of soil color is the determination of the effects of varying moisture content on the color and particularly on the color descriptions of various soils. Later it will of course be necessary to work out better terms to use in describing soils and to adopt color charts which may be used in the field. But the moisture problem must be solved first.

¹ Member of the Committee on Soil Color Standards of the American Association of Soil Survey Workers.

It is quite generally recognized that moisture exerts a very important influence on soil color. Soils in an air-dry condition are known to be lighter than when wet, the depth of color increasing with increases in moisture, up to a certain point. It is believed also that dark colored soils show greater change in color with variations in moisture, than do light colored types. However, the real effect of moisture on soil color has not been determined and it is not known whether or not there is any definite relation between the two.

The purpose of the work reported in this paper was to study briefly and preliminarily the effect of varying moisture content on the actual color of two soil types which occur rather extensively in Iowa. The differences in color are shown in plate 1. The variations in descriptions, using the colors given by Ridgway (2) are shown in the tables.

TABLE 1
Clinton silt loam

MOISTURE CONTENT per cent	COLOR OF SURFACE SOIL (RIDGWAY'S COLORS)	COLOR OF SUBSOIL (RIDGWAY'S COLORS)
Air-dry	Avellaneous, <i>slightly yellow</i>	Warm buff
10	Tawney Olive, <i>slightly light</i>	Cinnamon buff
20	Saccardos Umber, <i>slightly light</i>	Tawney olive, <i>slightly light</i>
30	Saccardos Umber, <i>slightly dark</i>	Tawney olive
40	Saccardos Umber, <i>slightly dark</i>	Tawney olive

TABLE 2
Tama silt loam

MOISTURE CONTENT per cent	COLOR OF SURFACE SOIL (RIDGWAY'S COLORS)	COLOR OF SUBSOIL (RIDGWAY'S COLORS)
Air-dry	Drab, <i>slightly dark</i>	Pinkish buff
10	Buffy Brown, <i>dark</i>	Clay color, <i>light</i>
20	Olive Brown, <i>dark</i>	Tawney olive, <i>dark</i>
30	Clove Brown, <i>light</i>	Saccardos umber
40	Clove Brown, <i>light</i>	Saccardos umber

The soils studied were the Clinton silt loam, a light colored type and the Tama silt loam a dark colored soil. Both soils are of loessial origin, the former being formed under timbered conditions, while the latter has developed on the prairies. Samples of these soils were chosen which were as closely typical of the types as it is possible to secure.

The colors of the surface soil and of the subsoil samples were carefully noted under uniform light conditions. The colors were determined on the air-dry soils and on samples containing 10, 20, 30 and 40 per cent moisture. Considerable difficulty was experienced in selecting terms from Ridgway's colors which really expressed the color of the soils. There seems to be too wide an interval between the colors given by Ridgway to permit of definite description.

Thus the color of the surface soil of the Clinton silt loam in an air-dry condition was nearest *Avellaneous* but there was a slightly yellowish cast to the color. With 10 per cent moisture, the color of the soil was slightly light for Ridgway's *Tawney Olive*. In the tables therefore, Ridway's terms are modified to fit more closely the soil colors.

The reproduction of the various colors was accomplished with considerable difficulty by the use of oils and many attempts were made before the colors could be reproduced accurately. With experience, excellent results could undoubtedly be secured more readily.

Examining the results given in the tables and in the figures, it will be noted that with both soils, the color becomes darker as the moisture content increases until 30 per cent is reached. Beyond that point there is little change. It is interesting to note that the Clinton silt loam, with 20 per cent of moisture resembles closely the Tama silt loam in an air-dry condition. When it contains 30 per cent moisture it is very nearly the color of the Tama with 10 per cent. If this is true for soils which are typical, it can readily be conceived that there might be a greater overlapping when variations within the soils are considered. For example the darkest Clinton silt loam and the lightest Tama would overlap much further when the moisture content was different. Other soil types likewise might show marked similarity with different conditions of moisture whereas they would be quite different when in an air-dry condition.

Of course the field man makes some allowance for the ever-changing moisture factor but it is extremely doubtful if men can consistently do this from month to month and year to year with nothing more tangible to check against than their own individual interpretation of color descriptions.

The degree of color change between the soil in an air-dry condition and with 10, 20 and 30 per cent moisture is more pronounced in the case of the Tama silt loam than with the Clinton. This would seem to indicate that the darker colored soils or those richer in organic matter show greater variations in color with changing moisture conditions. The color change however is not uniform. Not only is the color darkened with more moisture but different shades and tints are brought out. This is more noticeable in the light colored soil.

It seems evident from this brief study that the moisture factor may play a most important part in determining the color of soils and in the descriptions which are given in the survey reports. The need for a definite understanding of the significance of the moisture factor in field soils when they are being mapped is obvious. The field men should probably be provided with color charts showing the color of the typical soils with varying moisture content, 10, 20 and 30 per cent, and also air-dry. In this way the personal equation factor would operate only to the extent that the surveyor would need to judge of the moisture content. This he could undoubtedly do quite accurately and certainly he would be able to fix the soil color much more definitely than if he is obliged to guess at the probable color of the soil, if the moisture content were

lower or higher, as it might have been a day or two previous. Perhaps with further study, it may be possible to fix on definite colors with 10 and 30 per cent moisture, the intermediate content not being of sufficient effect to warrant consideration. If this is possible, the problem will be much simplified for these amounts would be easily translated by the field man into "dry" and "moist" and he could readily make a differentiation. Further work is of course necessary before such a solution of the problem of moisture and soil-color is possible. The effects of smaller differences in moisture than those used here must be tested. A wide variety of soils must be examined as the types used in this work may not indicate the results which may be secured with other light colored and dark colored soils. Further, more comprehensive study of moisture effects on soil color is certainly very desirable.

The adoption of more definite terms for describing soil color is also quite evidently necessary. Ridgway's color standards are good as far as they go but the differences between his colors are too great. Then, too, the terms which he uses are cumbersome, meaningless and useless from the practical standpoint. The color names selected by the Color Standards Committee of the American Association of Soil Survey Workers are much better but they are not nearly complete enough to be satisfactory. It is hoped that further work by this committee may lead to the adoption of a complete and reasonably simple method of describing soil colors.

Definite conclusions of course cannot be drawn from the meager data presented here but it is hoped that the report may serve to stimulate further study along this line and to hasten the time when soil colors may be more definitely described and the field men may experience less difficulty in mapping soils and in describing them.

REFERENCES

- (1) BROWN, P. E., AND O'NEAL, A. M. 1923 The color of soils in relation to organic matter content. Iowa Agr. Exp. Sta. Res. Bul. 75.
- (2) RIDGWAY, R. 1912 Color Standards and Color Nomenclature. Mrs. J. E. Ridgway, Olney, Ill.

THE EFFECT OF MOISTURE ON SOIL COLOR
A V O NAL

PLATE 1

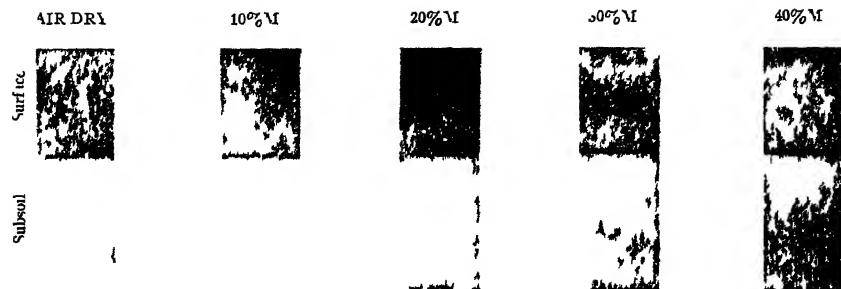


FIG. 1. CLINTON SILT LOAM



FIG. 2. TAMA SILT LOAM

ORGANIC PHOSPHORUS OF SOILS¹

J. T. AUTEN

Iowa Agricultural Experiment Station

Received for publication June 14, 1923

The amounts of organic phosphorus in soils are so considerable that their significance and possible application to practical agriculture cannot be overlooked. When 30 to 40 per cent of the total soil phosphorus is found in organic combination, its importance becomes apparent (3). The compounds in which phosphorus is combined in plants are quite well known and have been the starting point for several theories as to their final transformation; however, aside from the isolation of nucleic acid by Shorey (19) and lecithin by Aso (2), practically nothing has been done in the way of their identification in soils.

Very large amounts of organic phosphorus must be added to soils each year from plant growth. Nucleic acid is an important constituent of every living cell. Maclean (12) states that the phosphatides appear to be present in every animal and vegetable cell so far investigated. However, Plimner (15) in classifying the organic phosphorus compounds says "Phospholipins of which lecithin is the principal one, occur chiefly in animals and only to a small extent in plants." Aso (2) in summing up his work on organic phosphorus compounds in soils says "The quantity of lecithin is small so it cannot be taken into serious consideration." So far phytin has not been isolated from soils. Quite large amounts of this compound occur in seeds. Suzuki and Yoshimura (22) found 85 per cent of the phosphorus in clover to be phytin. Briefly then quite large amounts of nucleic acid and phytin and relatively small amounts of phosphatides are added to soils.

Gortner and Shaw (8) suggested that part, if not all, of the organic phosphorus compounds found in soils was extracted from living bacteria or protozoa.

Waksman (23), (24) found the highest bacterial number of any time of the year was 21,700,000 per gram of soil; ciliates and amoeba, 10 to 100 per gram; and flagellates 1,000 to 10,000 per gram. Waksman and Curtis (25) found the average number of actinomycetes to be 933,000 per gram. Calculating the weight of all the bacteria in the surface soil of an acre according to the figures given by Marshall (14) and using 1.3 per cent phosphorus as an average on the dry weight, only approximately .09 pounds of phosphorus can be accounted for. Using Marshall's figures again, and calculating the volume of organisms necessary to represent 300 pounds of organic phosphorus, there would be required in the surface alone a solid layer of living organisms 2.64 inches deep over the entire acre. Carrying the *reductio ad absurdum* still farther to include all organisms, assuming a 20 per cent dry matter content and a 1.3 per cent phosphorus content, there would be required for the 1566.22 pounds of organic phosphorus in all three depths of soil no. 4 (3) a solid layer of living organisms over 3 inches thick covering

¹ The author feels indebted to Dr. P. E. Brown for helpful suggestions in correcting and editing this manuscript; also to Dr. Paul Emerson and Dr. H. W. Johnson for many kind and pertinent suggestions during the carrying out of this work.

the entire acre. The latter allows for no space between organisms. If this be taken into account, the figures would necessarily be greater. Some large amounts of organic phosphorus are found in poor soils where the bacterial count would be low and in subsoils where it is generally conceded that living organisms are few. There must be some other source of organic phosphorus than living organisms.

Moreover, the ease of hydrolysis of nucleic acid, phytin, and lecithin would seem to eliminate them from consideration as making up any considerable portion of the large amount of organic phosphorus found in some cases. Nucleic acid is easily hydrolyzed by certain organisms (10). Lecithin is easily broken down by acids or bases, and phytin is quickly hydrolyzed by phytase (1). Then, too, nucleic acid, phytin, and lecithin are readily available to plants (20), which fact further removes them from consideration as a possible form of accumulated unavailable phosphorus.

It has been a rather generally accepted fact that soil organisms serve as a medium for storage of plant food. In reality it is doubtful if they are very important in this way. Even if their entire mass contained enough plant food to be of consequence it would be in the living organism and unavailable at the time when the plant most needed it.

It has been suggested by Potter and Benton (16) that perhaps the accumulation of organic phosphorus was due to pyrimidine nucleotides. This theory originated because of the similarity of the curves of hydrolysis of nucleic acid and ammonia extracts of soil. The theory was further substantiated by Schollenberger (18). No attempt has been made to determine nucleotides or nucleic acid in soil quantitatively. Funatsu (7) incubated nucleoprotein from beer yeast in sand cultures and found only 39 per cent of the phosphorus hydrolyzed in two months. The fact that nucleic acid was found in soils speaks well for the technique of the investigators and was a splendid piece of work, but in view of the very small amounts of nucleic acid or of its hydrolytic products, the purines and pyrimidines and in consideration of facts to appear later in this paper, there seems to be good evidence to indicate that nucleic acid does not accumulate in soils, either as such or as the pyrimidine half of the molecule.

Although Fraps (6) rendered untenable the assertion of Stewart (21) that the increase in soluble phosphorus after heating is organic and quantitative it seems that, although perhaps not absolutely quantitative, Schmoeger's (17) idea that heating liberated phosphorus from organic combination, has good foundation.

Briefly summing up the generally accepted facts based on work done up to this time:

1. Organic phosphorus in considerable amounts exists in soils.
2. An apparently satisfactory method for estimating organic phosphorus in ammonia extracts has been developed.
3. Phosphorus exists in soils as phospholipins, nucleic acid, and considering the amounts added probably as some phytin; perhaps, also, as an accumulation of pyrimidine nucleotides.

EXPERIMENTAL

The following experiments were carried out with the idea of making a critical study, first, of the method of Potter and Benton; second, to determine whether organic phosphorus in soils is in chemical combination or adsorbed; third, to discover if possible the nature of the organic phosphorus compounds.

The soil selected was Jackson silt loam. This particular soil was selected because of its high content of organic phosphorus; then, too, because of its low organic matter content it gave a more easily filterable ammonia extract. The soil is described as follows: "The surface soil is a light-brown, smooth, silt loam to a depth of 8-12 inches and passes into a yellowish-brown silty clay loam to silty clay. The subsoil is rather compact." The application of lime where the soil is acid and of phosphorus and organic matter gives good results.

In this section of the experimental work 200 gm. of soil were shaken for one hour with 1 per cent hydrochloric acid, filtered, washed, dried, reground, and shaken for 8 hours with 500 cc. of 4 per cent ammonia. The soil was separated from the extract by means of a separator running at a speed of 20,000-25,000 R.P.M. The method of determining organic phosphorus on this extract was that used in the previous experiments (3).

It has been noted that phosphorus is separated from guanine with some difficulty when isolating the purines or nucleic acid. It was thought possible that the purines or pyrimidines, existing in soils as a result of the hydrolysis of nucleic acid, might be dissolved in the ammonia extract and, when magnesia mixture was added, form, with the organic matter, a complex magnesium purine or pyrimidine phosphate. The inorganic phosphorus would thus be removed from solution in a form which would not be redissolved by dilute nitric acid and in consequence be calculated as organic. In order to test this supposition, various amounts of the purine and pyrimidines (isolated from yeast nucleic acid) were added to 100 cc. portions of the ammonia extract and the usual procedure for determining organic phosphorus carried out. The precipitates from magnesia mixture after having been washed with dilute nitric acid were analyzed for total phosphorus by the usual magnesium nitrate method. Such a voluminous precipitate was secured and it was of such a nature that although the washing with nitric acid was thorough, some inorganic phosphorus undoubtedly was left in an adsorbed state. The results secured can be considered only as comparative. The experiment was repeated using only guanine and xanthine. Concordant results were secured; but there was not enough difference to warrant the assumption that an organic phosphorus compound was formed during the precipitation with magnesia mixture. In fact in the first experiment the purines seemed to increase the magnesia precipitate while in the second the guanine seemed to increase the amount of inorganic phosphorus.

Table 1 shows the original experiment; table 2 the amino purine and oxy-purine test. It might well be stated that the results for phosphorus here as well as elsewhere in this paper are given in their equivalent in cubic centimeters of 0.1 N alkali. The total phosphorus on 100 cc. of extract was equivalent to 53.4 cc. of 0.1 N alkali. The 25 cc. of phosphate solution was equivalent to 24.4 cc. of 0.1 N alkali. In table 5, 10 cc. of phosphate solution equivalent to 9.76 cc. of 0.1 N alkali were used. The purine and pyrimidines were prepared from yeast nucleic acid according to the Jones method (11). In the removal of picric acid from adenine it was found that a more satisfactory separation than the ether-acid procedure was secured by dissolving the adenine picrate in ammonia, precipitating it with silver nitrate, washing and then boiling the well washed adenine silver salt with hydrochloric acid. The filtrate contained a known amount of the chloride and was diluted to the required volume. Choline was prepared from egg lecithin by hydrolysis with baryta, precipitation with platinum chloride, and subsequent separation with hydrogen sulfide.

TABLE 1

Effect of various amounts of organic bases on the phosphorus content of the washed magnesia mixture precipitate

BASE ADDED TO 100 CC. SOIL EXTRACT PLUS 25 CC. PHOSPHATE SOLUTION*			PHOSPHORUS AS 0.1 N ALKALINE EQUIVALENT
Kind	Amount	mgms.	cc.
		75	41.8
Adenine.....	50	39.7	
	5	38.7	
Guanine.....	100	40.4	
	50	37.1	
	5	39.9	
Uracil.....	100	40.6	
	50	42.1	
	5	43.1	
Cytosine.....	100	42.6	
	50	44.1	
	5	43.0	
Choline.....	100	43.5	
	50	43.8	
	5	46.7	
Xanthine.....	100	49.0	
	25	45.9	
	5	45.1	
Hypoxanthine.....	100	43.5	
	50	47.0	
	5	44.0	
None.....			46.4

* 25 cc. standard phosphate solution was equivalent to 24.4 cc. 0.1N alkali.

TABLE 2

Phosphorus in HNO₃ extract of magnesia mixture precipitate

SOIL EXTRACT	BASE ADDED		PHOSPHATE SOLUTION ADDED*	PHOSPHATE EQUIVALENT IN 0.1 N ALKALI
	Kind	Amount		
cc.		mgms.	cc.	cc.
100	Guanine	50	10	21.3
100	Xanthine	50	10	19.4
100	None	None		10.2

* 10 cc. standard phosphate solution was equivalent to 9.76 cc. 0.1N alkali.

The experiment shows that it is unlikely that the purines or pyrimidines, even if present in the soil in large amounts, would influence the determination of organic phosphorus.

In order to determine whether phosphorus was held in chemical combination in the ammonia extract or was simply adsorbed by colloids, equal amounts of the soil extract were treated with varying amounts of standard phosphate solution. The dilute nitric acid filtrate, the washed residue and the first filtrate from the magnesia precipitation were analyzed separately for phosphorus. Table 3 gives the results. It may be seen that complete recovery was made of the phosphorus added. There was no increase in the phosphorus in the residues and the first filtrate showed a constant amount. It must be concluded that appreciable adsorption did not take place or complete recovery of the added phosphorus would not have resulted. Because of the increased concentration of phosphorus there would have been a difference between the 25 cc. application and the 50 cc. application.

TABLE 3
Effect of adding phosphorus in different concentrations

SOIL EXTRACT*	STANDARD PHOSPHATE SOLUTION ADDED†	PHOSPHORUS EQUIVALENT IN CC. 0.1 N ALKALI		
		HNO ₃ filtrate	Washed residue	First filtrate
cc.	cc.	cc.	gm.	cc.
50	25	29.4	14.7	6.7
50	50	53.9	14.8	6.7

* 50 cc. soil extract contains 5.1 cc. phosphorus equivalent in 0.1N alkali.

† 25 cc. standard phosphorus contains 24.4 cc. phosphorus equivalent in 0.1N alkali.

50 cc. standard phosphorus contains 48.8 cc. phosphorus equivalent in 0.1N alkali.

There is another possibility in connection with the precipitation of inorganic phosphorus from ammonia extracts and that is the difference in precipitating agents. It was decided to try out varying amounts of magnesia mixture in order to determine if the mass action of an increased magnesium ammonium content would increase the amount of inorganic phosphorus precipitated. Saturated solutions of ammonium chloride and ammonium nitrate were also used as precipitants with interesting results.

Table 4 shows the results secured with different amounts of magnesia mixture and with saturated solutions of ammonium chloride and ammonium nitrate. Figures for the inorganic phosphorus in the dilute nitric acid filtrate as well as for phosphorus on the washed magnesia mixture precipitate and on the first filtrate from the magnesia mixture precipitate are given. In column 3 are the figures for the amounts of inorganic phosphorus found in the filtrates from ammonium chloride and ammonium nitrate precipitations. Table 4 shows that the amount of magnesia mixture has very little effect in increasing the amount of inorganic phosphorus. In the case of the 10 cc. addition, the small amount affected the distribution between the nitric acid insoluble organic and the soluble organic in the filtrate. The inorganic phosphorus con-

tent was not different from that secured by the addition of the large amounts. Very interesting results may be observed in the case of the ammonium salts. Here practically all of the inorganic phosphorus has been salted out along with the organic compounds. Very different results were anticipated; namely, that very little inorganic phosphorus would have been precipitated and much organic; but just the opposite occurred. Almost complete precipitation of inorganic phosphorus was accomplished. The phosphorus which remained after filtration from the ammonium salts was equivalent to only 0.3 cc. 0.1 N alkali, in the case of ammonium chloride, and 0.55 cc. in the case of ammonium nitrate. The surprising thing about this precipitation with ammonium salts was the large amount of organic phosphorus left in solution as compared with that left in the case of magnesia mixture (a 22-cc. equivalent against a 6-cc. equivalent in the case of the extract precipitated with 50 cc. of magnesia mixture), nearly four times as much. Evidently magnesia mixture is a precipitant of the organic compounds but it failed to precipitate any of the large

TABLE 4
Effect of different precipitants in varying amounts

PRECIPITANT	PHOSPHORUS GIVEN IN TERMS OF 0.1 N ALKALI			
	Inorganic phosphorus	Phosphorus in first filtrate	Inorganic phosphorus in filtrate from ammonium salts	Phosphorus in residues
	cc.	cc.	cc.	cc.
10 cc. magnesia mixture.....	9.65	8.35		35.4
25 cc. magnesia mixture.....	9.30	6.4		37.7
50 cc. magnesia mixture.....	9.9	6.0		37.5
100 cc. magnesia mixture.....	9.1	6.8		37.3
Saturated NH_4Cl	8.45	22.0	0.3	22.95
Saturated NH_4NO_3	8.95	22.0	0.55	22.45

remaining amount after the salting out with ammonium salts. These facts prove quite conclusively that the phosphorus in ammonia extracts of soil is largely organic for were it inorganic it would have been precipitated by magnesia mixture even though large amounts of ammonia salts were present. The removal of so much troublesome organic material by salting out with ammonium salts, leaving so large a proportion of the organic phosphorus in the filtrate suggests a possible means of isolation of some of the organic phosphorus compounds; namely, dialysis of the ammonium salts and crystallization following evaporation and solution in suitable solvents.

There seems to be no tendency for large amounts of magnesia mixture to increase the amounts of inorganic phosphorus. The variation in individual tests is so large that further work on a large number of samples will be necessary in order to settle this point. Any difference, however, is probably small.

The precipitate formed by adding magnesia mixture to ammonia extracts is so voluminous in some cases and of such a nature that the possibility of its

adsorbing and enclosing phosphorus between its finely divided particles is worthy of consideration. One hundred cubic centimetres of ammonia extract was precipitated with magnesia mixture and the precipitate thoroughly washed with dilute nitric acid as in the regular method. The residue on the paper was shaken up with dilute nitric acid in an Erlenmeyer flask and again filtered and washed. This residue was then allowed to stand covered with 100 cc. of distilled water for 24 hours. At the end of this time it was filtered and inorganic phosphorus very carefully determined on the filtrate. The residue was again allowed to stand with 100 cc. of distilled water for 10 days; then for six weeks. The inorganic phosphorus which diffused out is shown in table 5.

It may be seen that in the case of sample 1 an amount of inorganic phosphorus equivalent to 4.5 cc. 0.1 *N* alkali was diffused out of the precipitate. This of course in the regular procedure would be counted as organic. There is the possibility of this phosphorus having been hydrolyzed from the organic phosphorus compounds, inasmuch as the precipitate enclosed some nitric acid from the dilute nitric acid wash. The acid concentration in the second and

TABLE 5
Inorganic phosphorus diffused from washed residues

SAMPLE	0.1 <i>N</i> ALKALI EQUIVALENT TO PHOSPHORUS DIFFUSED			
	First period (48 hours)	Second period (10 days)	Third period (6 weeks)	Total
1	cc. 1.9	cc. 1.4	cc. 1.2	cc. 4.5
2	cc. 1.9	cc. 1.7	cc. 1.1	cc. 4.7
3	cc. 1.8	cc. 1.3	cc. 0.0	cc. 3.1

third periods, however, was very low. From an analytical point of view the presence of this phosphorus indicates the necessity of using an ammonia extract representing as small an amount of soil as is practical thus avoiding the voluminous precipitate. This inorganic phosphorus recovered represents 12 per cent of the total contained in the washed magnesia mixture precipitate. If it is hydrolyzed from organic compounds it would not necessarily indicate an ease of hydrolysis of such compounds in soil inasmuch as the precipitation and various washings have changed its nature and probably freed it from retarding enzymatic factors. Old infertile soils sometimes have high ratios of organic to inorganic phosphorus which indicate a low availability of organic phosphorus. The probabilities are that the 12 per cent recovered was largely inorganic adsorbed or enclosed.

When the possibilities of organic phosphorus being in soils as nucleic acid, phytin, and lecithin are considered, the question immediately arises as to the rates of hydrolysis of these compounds. Are they able to withstand bacterial activities? In the case of nucleic acid is the pyrimidine half of the molecule resistant to enzymes? In order to settle this point, nucleic acid, phytin, and

lecithin were incubated in silica sand with soil infusion. The sand had previously been digested for several days with hydrochloric acid, washed free of acid, and dried. By analysis it showed 99 per cent SiO₂.

Table 6 shows the results. One hundred milligrams of nucleic acid, 100 mgm. of phytin, and an amount of lecithin in absolute ether equivalent to 79.2 cc. 0.1 N alkali were mixed with 100 gm. of silica sand. The nucleic acid contained no inorganic phosphorus precipitable with magnesia mixture. The 100 mgm. phytin contained phosphorus equivalent to 3.3 cc. 0.1 N alkali. The lecithin contained in 20 cc. of the ether solution, inorganic phosphorus equivalent to 12 cc. 0.1 N alkali. The inoculated silica sand cultures were allowed to incubate at room temperatures and the inorganic phosphorus determined at one month intervals.

The method used for determining inorganic phosphorus in nucleic acid cultures consisted in adding ammonia and 25 cc. of magnesia mixture and after standing over night filtering off the unchanged nucleic acid. The residue was thoroughly washed with water containing ammonia; then the inorganic magnesium ammonium phosphate was dissolved out with dilute nitric acid, the

TABLE 6
Hydrolysis of organic phosphorus compounds

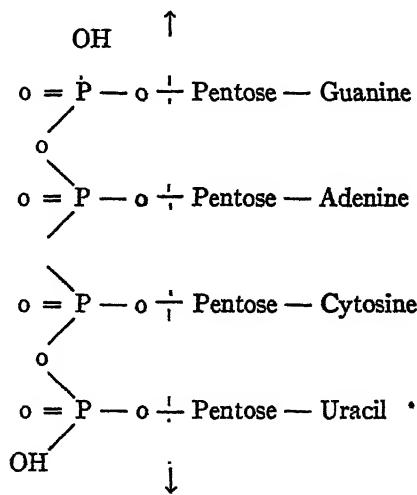
COMPOUND	AMOUNT HYDROLYZED AT END OF		
	First month	Second month	Third month
	per cent	per cent	per cent
Nucleic acid.....	80.7	85.6	85.04
Phytin.....	39.3	64.9	67.00
Lecithin.....	56.9	59.8	66.00

solution thoroughly oxidized and the phosphorus determined in the usual way by molybdate precipitation. Phytin was determined by the acid alcohol method of Forbes (5). It was necessary to work out a method for lecithin, and this was done as follows. Lecithin is insoluble in acetone. By using 10 cc. of nitric acid (sp. gr. 1.42) per liter of acetone, a solvent was found which proved very successful in dissolving the inorganic phosphorus and any glycerophosphoric acid. The mixtures of glycerophosphoric acid and phosphoric acid were taken as a measure of the hydrolytic power of the soil. The method was tested out as follows. Commercial lecithin was dissolved in alcohol, precipitate with acetone, dried and dissolved in absolute ether. Five cubic centimetres of this solution were added to about 50 gm. of silica sand and allowed to evaporate. The dried silica sand was then extracted with the acid acetone. An amount of inorganic phosphorus equivalent to 3 cc. of 0.1 N NaOH was obtained in the filtrate. Another 5-cc. portion of lecithin solution in sand was extracted with pure acetone and the extract evaporated. The residue was oxidized with nitric acid and the resulting solution after dilution and filtration tested for phosphorus in the usual way. An amount of phosphorus

equivalent to 3 cc. 0.1 *N* NaOH was secured. This showed that the short extraction with acid acetone did not hydrolyze any appreciable amount of the lecithin. The small amount of inorganic phosphorus found in each case was evidently left from the purification process or hydrolyzed subsequently. In order to test the solubility of inorganic phosphorus in acid acetone, 25 cc. of standard phosphate solution, equivalent to 21.1 cc. 0.1 *N* NaOH was evaporated to dryness and mixed with silica sand. Five cubic centimeters of lecithin solution in ether was next added and allowed to evaporate. Extraction of this sand mixture with acid acetone showed a complete recovery of both the inorganic phosphorus in the lecithin equivalent to 3 cc. 0.1 *N* NaOH and that in the standard equivalent to 21.1 cc. 0.1 *N* NaOH.

Table 6 shows that at the end of three months 85.04 per cent of the phosphorus of nucleic acid has been changed to the inorganic form, 67 per cent of the phytin phosphorus, and 66 per cent of the lecithin phosphorus.

Plant nucleic acid written structurally is shown below.



- . The horizontal dotted line divides the molecule into purine and pyrimidine nucleotides. The vertical line shows how phosphorus splits off on hydrolysis giving phosphoric acid and nucleosides. The latter process is probably what occurs in soils. The theory that pyrimidine nucleotides remain as such in soils cannot be a general truth for in the case of the incubation mentioned at least 70 per cent of the pyrimidine phosphorus has been split off from the molecule. In the case of phytin and lecithin the hydrolysis proceeded rapidly and probably in soils under conditions of drainage and aeration would rapidly approach completion. No doubt there are always small amounts of all three compounds in most soils. Nucleic acid has unquestionably been isolated as has lecithin, though in small amounts. Phytin has so far not been isolated. None of these compounds or their hydrolytic products are difficult to isolate

if present in large quantities. Were 300 pounds of phosphorus to be calculated to either of the pyrimidine nucleotides, there would be about 3000 pounds of cytosine or uracil nucleotide in an acre representing 1000 pounds of either cytosine or uracil. Were the bases in equal amounts, there would be 500 pounds of each in the surface soil of an acre, an amount which could not fail of detection.

Twenty kilograms of Jackson silt loam were extracted with ammonia following HCl extraction and the ammonia extract hydrolyzed with sulfuric acid. The resulting hydrolyzed mixture was treated for the isolation of purines and pyrimidines. The characteristic silver purine and pyrimidine precipitates were noted, but the amounts were so small as to render isolation and identification impossible. Hypoxanthine was isolated in very small amounts from the hydrochloric acid extract.

Maillard (13) in 1912 found that carbohydrates and amino acids may be condensed to form a humus-like substance. This artificial humus is soluble in ammonia and may be reprecipitated by acids. The following experiment was conducted to ascertain whether phosphorus, too, could be made to combine in the condensation product. Sixteen grams dextrose, 4 gm. alanine, 0.5 gm. $\text{Na}_2\text{HPO}_4 \cdot 12 \text{H}_2\text{O}$ and 16 gm. water were heated for 3 hours in a steam pressure oven at 25 pounds pressure. A dark brown brittle substance was obtained which was treated for organic phosphorus by the Potter and Benton method. The ammonia extract of this artificial humus was black and resembled the soil extract. One hundred cubic centimeters of it gave total phosphorus equivalent to 14.9 cc. 0.1 N NaOH. An equal aliquot contained inorganic phosphorus equivalent to 4.5 cc. 0.1 N NaOH. A large amount of the phosphorus had been condensed with the complex molecule and could not be precipitated with magnesia mixture.

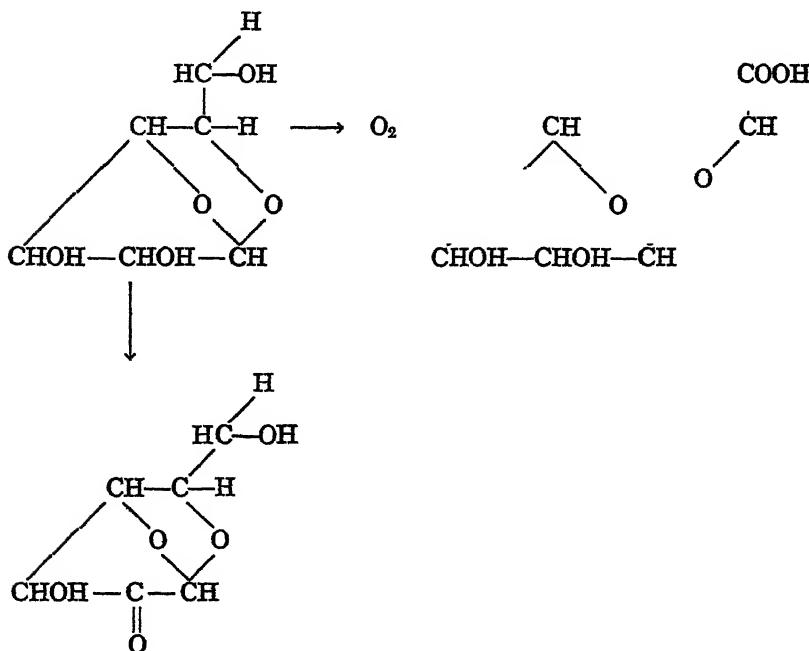
Dextrose and alanine refluxed for 15 hours at 100°C. gave the same black residue to which in ammonia solution phosphorus was added. Upon the addition of magnesia mixture the phosphorus was completely recovered. One hundred cubic centimetres of the same ammonia solution of artificial humus containing 25 cc. of standard phosphate solution was acidified with hydrochloric acid; then made alkaline with ammonia and precipitated with magnesia mixture. The same was repeated except that the standard phosphate solution was added after acidifying. In both cases complete recovery of phosphorus resulted. These tests were made to ascertain whether the phosphorus was absorbed from the acid solution as would be the condition in the preliminary acid extraction. Very probably the organic phosphorus is present in soils as the calcium, magnesium, iron, or aluminum salts of the phosphorus, carbohydrate, amino acid complex and not absorbed from the phosphoric acid liberated by the hydrochloric acid from inorganic phosphorus salts. There are two possibilities at least, (a) that the organic phosphorus is formed under conditions existing when the hydrochloric acid liberates inorganic phosphorus from inorganic salts or (b) that it exists as the calcium salt of the organic phosphorus

complex which when the calcium is removed becomes soluble because of the formation of the ammonium salt. It is a well known fact that without previous acid extraction ammonia will dissolve very little organic phosphoric acid; but after HCl extraction practically all of it is dissolved. It seems very reasonable to infer that the organic phosphorus exists as organic in the soil and is not formed under the conditions of the experiments.

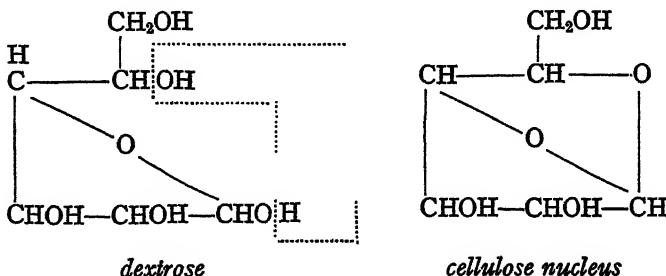
Another interesting observation was made of the artificial humus. Since the condensation between dextrose and alanine went on rather slowly at 100°C., tests were made from time to time. The product first formed was readily soluble in ammonia as well as in acids. As the condensation went on and the product became more and more complex, while it remained soluble in ammonia, it became insoluble in acids. At the end of the process the mixture might have been divided into three parts: ammonia insoluble, ammonia soluble but acid insoluble, and ammonia and acid soluble. The ammonia insoluble corresponds to humin, the ammonia soluble acid insoluble to humus, and the red acid soluble portion to Mulders apocrenic acid.

Beckley (4) has recently written a very interesting article on the formation of humus. He points out that cellulose broken down into its components is changed to hydroxymethyl furfural and this in turn condenses to form humus.

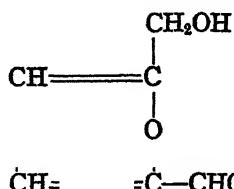
Hibbert (9) suggests a formula for cellulose and explains why oxycelluloses are either alkali soluble or alkali insoluble. His formulae below show how by oxidation the carboxy- or alkali-soluble oxycellulose is formed in one case and the ketonic or alkali-insoluble form in the other.



Hibbert also explains the process of changing cellulose to hydroxymethyl furfural. Cellulose hydrolyzes quantitatively to give dextrose. The relationship between dextrose and the cellulose nucleus Hibbert graphically represents as below.



By heating, cellulose is partially converted into w hydroxymethyl furfural



According to Beckley (4) humus is formed by polymerization or condensation of this compound. We can then easily follow the formation of humus from cellulose. It is not difficult to conceive of a complex condensation product which has both hydroxyl groups and carboxyl groups and which might easily condense or combine with phosphoric, sulfuric or other acids and at the same time form a calcium salt. It seems very likely that humus is such a complex. As humus ages it becomes more complex. Phosphoric acid and other elements become buried, so to speak, in the complex molecule and as a consequence are less available. The liberation of phosphoric acid from the carbonaceous complex is probably dependent for the most part in the older humus to oxidation. In the younger formations no doubt hydrolysis plays a part. These deductions throw some light on the organic phosphorus situation. Phosphorus locked up in organic combination in old soils is less available and remains while the inorganic phosphorous and more available organic are used up by plants or leached; hence the increase in the ratio of organic to total. We may, too, explain the hydrolysis curve of ammonia extracts. The more simple complex gives up its phosphorus more readily than does the more complex; hence the similarity to nucleic acid.

CONCLUSIONS

1. Organic phosphorus exists in large amounts in soils and may be determined with a fair degree of accuracy by the Potter and Benton method.

2. Organic phosphorus probably does not exist in any considerable amount as nucleic acid, phytin, or lecithin.
3. Organic phosphorus in soils is probably not an accumulation of pyrimidine nucleotides.
4. Organic phosphorus compounds added to soils are probably hydrolyzed and the inorganic phosphorus combined in a calcium-magnesium or other metal salt of an organic amphoteric complex.

REFERENCES

- (1) ANDERSON, R. J. 1915 The hydrolysis of phytin by the enzyme phytase contained in wheat bran. *In Jour. Bio. Chem.*, v. 20, 475.
- (2) Aso, K. 1904 On organic compounds of phosphorus in soils. *In Bul. Col. Agr. Tokio Imp. Univ. (Japan)*, 6, p. 277-284.
- (3) AUTEN, J. T. 1922 The organic phosphorus content of some Iowa soils. *In Soil Sci.*, v. 13; p. 119-124.
- (4) BECKLEY, V. A. 1921 The formation of humus. *In Jour. Agr. Sci.*, v. 11, p. 69-77.
- (5) FORBES, E. B., LEHMANN, A., COLLISON, R. C., WHITTIER, A. C. 1910 Methods for the quantitative estimation of inorganic phosphorus in vegetable and animal substances. *Ohio Agr. Exp. Sta. Bul.* 215.
- (6) FRAPS, G. S. 1911 Organic phosphorus of soils. *Tex. Agr. Exp. Sta. Bul.* 136.
- (7) FUNATSU, T. 1908 On different forms of phosphoric acid in press Cake. *In Bul. of Col. of Agr. Tokio Imp. Univ. (Japan)*, v. 7; p. 457-459.
- (8) GORTNER, R. A., AND SEAW, W. M. 1916 The organic matter of the soil. IV. Some data on humus phosphoric acid. *In Soil Sci.*, v. 3, p. 99.
- (9) HIBBERT, H. 1921 The constitution of cellulose. *In Jour. Indus. and Engin. Chem.*, v. 13, no. 4, p. 334-342.
- (10) IWANOFF, L. 1903 Ueber die fermentative Zersetzung der Thymo-nuclinsaure durch Schimmelpilze. *In Zeitschr. Physiol. Chem.*, v. 39; p. 31.
- (11) JONES, W. 1914 Nucleic Acids, Their Chemical Properties and Physiological Conduct. *Monograph*, Longmans, Green & Co., New York.
- (12) MACLEAN, H. 1918 Lecithin and Allied Substances; The Lipins. *Monograph*, Longmans, Green and Co., N. Y.
- (13) MAILLARD, L. C. 1912 Formation d'humus et de combustible mineraux sans intervention de l'oxygene atmospherique, des micro-organismes, des hautes temperatures, ou des fortes pressions. *In Compt. Rend. Acad. Sci. (Paris)*, v. 155, p. 1554-1556.
- (14) MARSHALL, C. E. 1912 Microbiology, p. 89. P. Blakiston's Sons and Co., Phila.
- (15) PLIMMER, R. H. A. 1912 The Metabolism of Organic Phosphorus Compounds. Their Hydrolysis by Action of Enzymes. *Monograph*, Longmans, Green and Co., N. Y.
- (16) POTTER, R. S., AND BENTON, T. H. 1916 The organic phosphorus of soils. *In Soil Sci.*, v. 2, p. 291-298.
- (17) SCHMOEGER, M. 1893 Ueber den Phosphor in Moorböden. *In Ber. Deut. Chem. Gesel.*, Jahrg. 26, v. 1, p. 386.
- (18) SCHOLLENBERGER, C. J. 1918 Organic phosphorus of soils: Work on methods for extraction and determination. *In Soil Sci.*, v. 6, p. 365-395.
- (19) SHOREY, E. 1911 Nucleic acid in soils. *In Science*, n. s., v. 35, p. 390.
- (20) SCHREINER, O., AND SKINNER, J. J. 1912 Nitrogenous soil constituents and their bearing on soil fertility. U. S. Dept. Agr. Bur. Soils Bul. 87.
- (21) STEWART, ROBT. 1910 Quantitative relationship of carbon, phosphorus, and nitrogen in soils. *Ill. Agr. Exp. Sta. Bul.* 145.

- (22) SUZUKI, U., AND YOSHIMURA, K. 1907 Ueber die Verbreitung von Anhydro-Oxy-Methylen-Diphosphor Sauren oder "Phytin" in Pflanzen. *In* Bul. Col. Agr. Tokio Imp. Univ. (Japan), v. 7, p. 495-502.
- (23) WAKSMAN, S. A. 1916 Bacterial numbers in soils at different seasons of the year. *In* Soil Sci., v. 1, p. 363.
- (24) WAKSMAN, S. A. 1915 Studies on soil protozoa. *In* Soil Sci., v. 1, p. 140.
- (25) WAKSMAN, S. A., AND CURTIS, R. E. 1916 The actinomyces of the soil. *In* Soil Sci., v. 1, p. 99.

EQUILIBRIUM STUDIES OF SODIUM CARBONATES AND BICARBONATES IN SOME IDAHO SOILS

RAY E. NEIDIG AND HARRY P. MAGNUSON¹

Idaho Agricultural Experiment Station

Received for publication May 16, 1923

The question of the reclamation of many natural alkali soils and the prevention of soils already in cultivation from becoming "salted out" is one of paramount importance in all irrigated regions. The attempt to utilize land containing a considerable percentage of salts has led many investigators to study the relative toxicity of the various alkali salts toward numerous crops. At present the Idaho Agricultural Experiment Station is carrying on an extensive project dealing with the determination of the tolerance of various crops toward alkali under Idaho soil conditions. The earlier investigations on tolerance of crops for alkali were based on the assumption that the amount of alkali added to the soil was the criterion to be followed in judging tolerance. This view, however, has been greatly changed in latter years by the work of investigators who base their view on toxicity from the amount of salts recoverable in the soil extract rather than from the salts added.

The work of Headley, Curtis and Scofield (5) has shown that when sodium carbonate is added to a soil and allowed to remain in contact for several weeks that the total amount of recoverable salts, including both the normal carbonate and the bicarbonate, is much less than the quantity added. When two types of soils were studied, a sandy and a loam soil, they found that the amount of carbonate salts recoverable from the loam soil was very much less than that recoverable from the sandy soil, indicating a different amount of absorption² or retention of carbonates by soils of different chemical composition and physical structure. The great discrepancy between the amount of salts added and the amount of salts recoverable in the soil extract has led to conflicting statements in the literature on the relative toxicity of alkali salts when the toxicity is based on added salts rather than the recoverable salts.

Harris and Pittman (4), in their work with added alkali, mention the discrepancy between the amount of carbonate salts added to soils and the amount recoverable in a water extract, observing also that more injury resulted to plants when grown in sand than when grown in a loam soil, both receiving equal amounts of added sodium carbonate.

¹ The data in this paper have been submitted in thesis form to the faculty of the University of Idaho by Harry P. Magnuson in partial fulfillment of the requirements for the degree of Master of Science in Agriculture.

Published with the permission of the Director of the Idaho Agricultural Experiment Station.

² The term absorption is used in this paper to refer to all cases of retention of salts by the soil whether the phenomena be primarily absorption or adsorption as distinguished by some writers, or a combination of both.

Kearney (7) of the United States Department of Agriculture, Bureau of Plant Industry, studied the relative absorption of soil by sodium carbonate and sodium chloride and found that when equal amounts of sodium chloride and sodium carbonate were added to sand the amount of sodium carbonate in the solution from the sand was much less than the sodium chloride, using the electrical resistance method as a basis of comparison. It is evident from past experiments, therefore, that the actual toxicity of salts must be based on the amount of salt present in solution, in other words, recoverable salt rather than added salt.

Another point of interest brought out by Headley, Curtis and Scofield in their work with soil is that when sodium carbonate is added to a soil a considerable amount of sodium bicarbonate is recovered. Some of the normal carbonate is thus changed to bicarbonate. They state that the comparative toxicity of sodium carbonate and sodium bicarbonate is approximately the same when the total of the carbonate salts recoverable is considered rather than the percentage of salts added to the soil. In other words the toxicity of these salts in the soil is directly associative with the quality of the basic radical in the salts recoverable.

Kearney and Cameron (8) have shown that the bicarbonate salt of sodium is less toxic in water solution to white lupine than sodium carbonate. It has also been shown by Cameron and Briggs (2) that in water solutions of sodium carbonate, sodium bicarbonate is gradually formed until approximately one-half of the sodium carbonate is changed over to the sodium bicarbonate. It is evident, therefore, that in all alkali studies where normal sodium carbonate was used and the results of toxicity were based on salts added, an error was introduced owing to the reversion of some of the normal sodium carbonate to the sodium bicarbonate as well as the fact that soils withhold much of the sodium carbonate from the water extract. All these facts make it obvious that the toxicity of alkali should be judged by the salts recoverable rather than the salts added to the soil.

In our investigations dealing with tolerance of crops for alkali, preliminary work indicated that the amount of alkali salts, especially sodium carbonate that could be recovered in the water extract varied considerably with different soil types. It was thought of interest to determine for definite and widely different soil types as found in Idaho, the relative absorption or retention factor, if such it might be called, and also the amount of carbonate salts recoverable throughout stated intervals of time, i.e., this study concerned the equilibrium of the carbonate salts, sodium carbonate and sodium bicarbonate, as affected by these different soil types when in contact for a definite period of time under uniform moisture conditions.

It was also thought of practical importance to ascertain the effect of adding additional amounts of the carbonate salts to these soils after they had reached an apparent equilibrium as judged by the analyses of the soil extract and noting whether the soil would absorb or retain an additional amount of carbonate salts. The findings of this interesting phase of the investigation will be discussed later in the paper after the methods and data are introduced.

Preliminary studies with Idaho soils indicated that some of the soil types showed widely different physical and chemical properties. Various differences were also noted in their power of retaining carbonates when known amounts of carbonate salts were added to the soils. Three soils showing the widest differences in properties were selected for the experiment. They were, Palouse silt loam, Caldwell silt loam subsoil and Boise silt loam. The Boise silt loam consisted of two samples, one of which was comparatively free from natural alkali, while the other sample represented a soil containing considerable alkali salts consisting of chlorides and sulfates.

DESCRIPTION OF SOILS

The Palouse silt loam soil is a dark colored soil high in fertility and organic matter. When wet, this soil is black in color. The soil used in the experiment was taken from the first nine inches of surface soil on the Experiment Station plots at Moscow.

The Caldwell silt loam subsoil sample was taken at a depth of five feet in the Caldwell silt loam series. This subsoil is a grayish yellow, silty clay loam, and very compact. The sample was also taken from soil on the experimental farm.

The Boise silt loam samples were secured from southern Idaho near Parma and Caldwell. One sample containing considerable natural alkali salts of chlorides and sulfates, while the other contained very little alkali. The soil is a grayish colored light sandy loam and is soft and ashy to the touch, carrying a large amount of silt. The two Boise silt loam soils were secured from points approximately fifteen miles apart, and while they are both classified as Boise silt loam, they may differ slightly in their physical and chemical properties.

The four soils were examined for alkali salts and found to contain the following percentages expressed on the anhydrous basis.

SOIL TYPE	SODIUM CARBONATE <i>per cent</i>	SODIUM BICARBONATE <i>per cent</i>	SODIUM CHLORIDE <i>per cent</i>	SODIUM SULFATE <i>per cent</i>
Palouse silt loam.....	0.000	0.018	0.004	0.006
Caldwell silt loam.....	0.000	0.018	0.000	0.004
Boise silt loam.....	0.000	0.018	0.712	0.119
Boise silt loam.....	0.000	0.041	0.002	0.000

PREPARATION OF THE SOILS

A series of eight 1-gallon jars was filled for each of the four soils. To four jars in each series were added different amounts of the normal sodium carbonate salts, namely, 0.25, 0.5 1.0 and 1.5 gm. per 100 gm. soil calculated on the anhydrous soil basis. To the remaining four jars of each series were added amounts of sodium bicarbonate equivalent in each case to the amounts of normal carbonate salts used in the first series. The actual weights of sodium bicarbonate used were 0.4, 0.8, 1.6 and 2.4 gm. per 100 gm. anhydrous soil. These salts were thoroughly mixed with the soils on December 23, 1920, and a sample taken on the same day and analyzed for recoverable carbonate and bicarbonate salts by the method described later in this publication.

An additional series of experiments was carried out which had for its object the determination of the equilibrium of the carbonate and bicarbonate salts in these same soils when kept in an air-dry condition during the same periods as the soils to which water was added. A small portion of the air-dried soils mixed on December 23, 1920, was set aside for this purpose. These were also analyzed at stated intervals on November, 2, 1921 and February 7, 1923. The entire period of contact was a little over two years. The results are given in table 5.

METHODS USED

The estimation of the carbonate salts in the water extract was made by the methods described by the Bureau of Soils (2) with the exception that in this work the proportion of water to soil was ten to one instead of twenty to one. Congo red indicator was used instead of methyl orange due to the fact that extracts of some of the soils were dark in color which masked the end point when methyl orange was used as an indicator. Samples were taken from each jar by means of a soil tube. In this manner several cores, representing the entire depth of soil, were secured from each jar. These cores were very carefully mixed and a

composite sample taken for analysis. The soils sampled on December 23, 1920, and January 3, 1921, were dried before analyzing, but in all other samples the moist soil was analyzed directly, since drying was found to slightly change the equilibrium.

The soils were kept at a moisture content of approximately 20 per cent throughout the first series of the experiment which was from December 23, 1920 to July 26, 1921. Four samples of each soil were taken during this period; the first sample, on December 23, 1920, the date of mixing; the second, on January 3, 1921; the third on February 25, 1921; and the last, on July 26, 1921. After this last date the soils were allowed to air-dry. The data for this first equilibrium period are given in table 1 and also in figures 1-4.

Table 1 contains all the data on the carbonate salts added to the soil and carbonate salts recovered in the water extract for all periods included in the first series for the four soils. The additions of sodium bicarbonate are the molecular equivalents of the corresponding additions of normal sodium carbonate. The salts added and recovered are expressed as grams per 100 grams of anhydrous soil. The column headed total sodium carbonate equivalent represents the sum of the normal carbonate recovery and the bicarbonate recovery, which is calculated to its equivalent of normal sodium carbonate. Water extracts of soils made after adding bicarbonate salts showed an alkaline reaction to phenolphthalein, indicating a reversion to normal carbonate and possibly a small amount hydrolyzed to the hydroxide. Either compound would appear alkaline to phenolphthalein. In all the data, however, the results on this particular portion of the water extract are calculated as normal sodium carbonate.

The results of the first series indicated that the soils had reached a point where only a slight reduction in total recovery of soluble carbonate salts was noted when examined. At this point it was thought of interest to study the effect of adding a large quantity of carbonate and bicarbonate salts to each of these soils to ascertain whether the soils had reached their maximum capacity of absorption of these salts.

Hence to the same soils used in the first experimental period and which were allowed to become air-dry, additional amounts of sodium carbonate and sodium bicarbonate were added on August 10, 1921. One gram of sodium carbonate per 100 gm. anhydrous soil was added to the sodium carbonate group and 1.6 gm. sodium bicarbonate, to the sodium bicarbonate group of soils. In the second period therefore, the soils contain the original amount of carbonate salts which were added, together with the additional 1 per cent of sodium carbonate or the equivalent in sodium bicarbonate. This second addition marks the beginning of the second series, the results of which are given in table 2. The soils were sampled September 15, 1921, December 12, 1921, June 10, 1922, and October 19, 1922. The time between the first two samplings, it should be noted was a little less than fourteen and one-half months. The soils were kept at approximately fifteen per cent moisture content throughout the entire second period. The results are given in table 2 and figures 1-4.

All the results expressed in this paper, the reader should bear in mind, are calculated from the acid radicals HCO_3^- and CO_3^{2-} which were directly deter-

TABLE I

Carbonates added and recovered from soils maintained at optimum moisture content. First series

TEST NUMBER	SALTS ADDED PER 100 GM. ANHYDROUS SOIL		SALTS RECOVERED IN WATER EXTRACT PER 100 GRAMS OF ANHYDROUS SOIL											
			December 23, 1920			January, 3, 1921			February 25, 1921			July 26, 1921		
	Na ₂ CO ₃	NaHCO ₃	Na CO ₃	Na ₂ HCO ₃ expressed as Na ₂ CO ₃	Total Na ₂ CO ₃ equivalent	Na ₂ CO ₃	Na ₂ HCO ₃ expressed as Na ₂ CO ₃	Total Na ₂ CO ₃ equivalent	Na ₂ CO ₃	Na ₂ HCO ₃ expressed as Na ₂ CO ₃	Total Na ₂ CO ₃ equivalent	Na ₂ CO ₃	Na ₂ HCO ₃ expressed as Na ₂ CO ₃	Total Na ₂ CO ₃ equivalent
<i>Palouse silt loam</i>														
1	0.25		0.000	0.183	0.183	0.000	0.081	0.081	0.012	0.046	0.058	0.000	0.030	0.030
2	0.5		0.083	0.241	0.324	0.063	0.132	0.195	0.026	0.089	0.115	0.012	0.093	0.105
3	1.0		0.353	0.334	0.687	0.228	0.193	0.421	0.167	0.115	0.282	0.137	0.142	0.279
4	1.5		0.706	0.406	1.110	0.416	0.183	0.599	0.293	0.219	0.572	0.325	0.151	0.476
5		0.4	0.000	0.180	0.180	0.020	0.091	0.111	0.006	0.060	0.066	0.000	0.029	0.029
6		0.8	0.000	0.456	0.456	0.083	0.142	0.225	0.069	0.067	0.136	0.017	0.089	0.106
7		1.6	0.000	0.915	0.915	0.228	0.193	0.421	0.152	0.121	0.273	0.076	0.143	0.219
8		2.4	0.020	1.250	1.270	0.374	0.152	0.526	0.470	0.172	0.642	0.232	0.141	0.373
<i>Caldwell silt loam subsoil</i>														
9	0.25		0.062	0.153	0.215	0.062	0.091	0.153	0.074	0.052	0.126	0.048	0.041	0.089
10	0.5		0.187	0.122	0.309	0.162	0.091	0.257	0.146	0.047	0.193	0.123	0.032	0.155
11	1.0		0.644	0.122	0.766	0.374	0.040	0.414	0.288	0.079	0.367	0.207	0.059	0.266
12	1.5		0.852	0.132	0.984	0.644	0.010	0.654	0.385	0.079	0.464	0.292	0.048	0.340
13		0.4	0.000	0.213	0.213	0.083	0.071	0.154	0.072	0.062	0.134	0.048	0.046	0.094
14		0.8	0.042	0.427	0.469	0.166	0.071	0.237	0.184	0.054	0.238	0.111	0.048	0.159
15		1.6	0.104	0.862	0.906	0.395	0.010	0.405	0.313	0.067	0.380	0.260	0.069	0.329
16		2.4	0.124	1.180	1.304	0.770	0.050	0.820	0.551	0.133	0.684	0.548	0.067	0.615
<i>Boise silt loam containing natural alkali, chlorides and sulfates</i>														
17	0.25		0.041	0.101	0.142	0.020	0.071	0.091	0.024	0.046	0.070	0.010	0.033	0.043
18	0.5		0.124	0.091	0.215	0.083	0.081	0.164	0.051	0.043	0.094	0.049	0.053	0.102
19	1.0		0.623	0.000	0.623	0.270	0.101	0.371	0.270	0.029	0.299	0.152	0.047	0.199
20	1.5		0.873	0.061	0.934	0.624	0.010	0.634	0.536	0.103	0.639	0.358	0.099	0.457
21		0.4	0.000	0.233	0.233	0.020	0.071	0.091	0.060	0.026	0.086	0.005	0.033	0.038
22		0.8	0.000	0.456	0.456	0.062	0.091	0.153	0.073	0.029	0.102	0.057	0.038	0.095
23		1.6	0.020	0.781	0.801	0.250	0.091	0.341	0.207	0.081	0.288	0.165	0.062	0.227
24		2.4	0.083	1.078	1.161	0.520	0.010	0.530	0.535	0.015	0.550	0.345	0.123	0.468
<i>Boise silt loam free from alkali chlorides and sulfates</i>														
25	0.25		0.146	0.071	0.217	0.083	0.081	0.164	0.094	0.057	0.151	0.077	0.039	0.116
26	0.5		0.104	0.151	0.257	0.250	0.050	0.300	0.245	0.008	0.253	0.137	0.047	0.184
27	1.0		0.644	0.071	0.715	0.436	0.030	0.466	0.464	0.096	0.560	0.266	0.079	0.345
28	1.5		0.996	0.010	1.006	0.749	0.020	0.769	0.643	0.041	0.684	0.511	0.069	0.580
29		0.4	0.047	0.193	0.240	0.104	0.091	0.195	0.093	0.058	0.151	0.085	0.035	0.120
30		0.8	0.083	0.344	0.427	0.228	0.060	0.288	0.209	0.031	0.240	0.153	0.041	0.194
31		1.6	0.166	0.668	0.834	0.395	0.050	0.445	0.360	0.107	0.467	0.326	0.046	0.372
32		2.4	0.104	1.239	1.343	0.644	0.020	0.664	0.650	0.132	0.782	0.562	0.065	0.627

TABLE 2
Carbonates added and recovered from soils maintained at optimum moisture content. Second series

POD NUMBER	SALTS ADDED PER 100 GM. ANHYDROUS SOIL		SALTS RECOVERED IN WATER EXTRACT PER 100 GRAMS OF ANHYDROUS SOIL											
			September 15, 1921			December 12, 1921			June 10, 1922			October 19, 1922		
	Na ₂ CO ₃	NaHCO ₃	Na ₂ CO ₃	NaHCO ₃ expressed as Na ₂ CO ₃	Total Na ⁺ CO ₃ equivalent	Na ₂ CO ₃	NaHCO ₃ expressed as Na ₂ CO ₃	Total Na ⁺ CO ₃ equivalent	Na ₂ CO ₃	NaHCO ₃ expressed as Na ₂ CO ₃	Total Na ⁺ CO ₃ equivalent	Na ₂ CO ₃	NaHCO ₃ expressed as Na ₂ CO ₃	Total Na ⁺ CO ₃ equivalent
<i>Palouse silt loam</i>														
1	1.0		0.363	0.064	0.427	0.237	0.110	0.347	0.197	0.171	0.368	0.165	0.224	0.389
2	1.0		0.357	0.107	0.464	0.324	0.194	0.518	0.269	0.239	0.508	0.290	0.134	0.424
3	1.0		0.579	0.153	0.732	0.472	0.040	0.512	0.465	0.009	0.474	0.412	0.024	0.436
4	1.0		0.684	0.190	0.874	0.748	0.230	0.978	0.638	0.350	0.988	0.695	0.110	0.805
5		1.6	0.326	0.074	0.400	0.249	0.097	0.346	0.174	0.206	0.380	0.171	0.108	0.279
6		1.6	0.048	0.213	0.261	0.203	0.106	0.309	0.252	0.186	0.438	0.173	0.216	0.389
7		1.6				0.593	0.141	0.734	0.440	0.213	0.653	0.418	0.112	0.530
8		1.6				0.695	0.142	0.837	0.640	0.187	0.827	0.589	0.129	0.718
<i>Caldwell silt loam subsoil</i>														
9	1.0		0.495	0.117	0.612	0.487	0.079	0.566	0.368	0.023	0.391	0.345	0.019	0.364
10	1.0		0.470	0.105	0.575	0.714	0.068	0.782	0.498	0.038	0.536	0.512	0.000	0.512
11	1.0		0.700	0.064	0.764	0.666	0.000	0.666	0.462	0.060	0.522	0.448	0.000	0.448
12	1.0		0.841	0.081	0.922	0.690	0.044	0.734	0.471	0.056	0.527	0.408	0.014	0.422
13		1.6	0.353	0.108	0.461	0.256	0.071	0.327	0.323	0.047	0.370	0.311	0.020	0.331
14		1.6	0.681	0.098	0.779	0.481	0.064	0.545	0.432	0.184	0.616	0.335	0.019	0.354
15		1.6	0.876	0.163	1.039	0.885	0.077	0.962	0.860	0.000	0.860	0.790	0.015	0.805
16		1.6	1.455	0.165	1.620	1.214	0.055	1.269	1.045	0.032	1.077	1.002	0.059	1.061
<i>Boise silt loam containing natural alkali, chlorides and sulfates</i>														
17	1.0		0.491	0.042	0.533	0.496	0.063	0.559	0.324	0.032	0.356	0.235	0.069	0.304
18	1.0		0.510	0.115	0.625	0.485	0.082	0.567	0.371	0.067	0.438	0.374	0.000	0.374
19	1.0		0.841	0.021	0.861	0.734	0.081	0.815	0.628	0.000	0.628	0.650	0.039	0.689
20	1.0		1.322	0.000	1.322	1.030	0.081	1.111	0.842	0.000	0.842	0.835	0.093	0.928
21		1.6	0.463	0.077	0.540	0.294	0.063	0.357	0.276	0.050	0.326	0.228	0.058	0.286
22		1.6	0.624	0.108	0.732	0.456	0.130	0.586	0.400	0.005	0.405	0.330	0.051	0.381
23		1.6	0.924	0.225	1.149	0.814	0.104	0.918	0.674	0.000	0.674	0.621	0.098	0.719
24		1.6	1.121	0.071	1.192	1.000	0.013	1.013	0.824	0.000	0.824	0.836	0.048	0.884
<i>Boise silt loam free from alkali chlorides and sulfates</i>														
25	1.0		0.543	0.078	0.621	0.459	0.204	0.663	0.456	0.000	0.456	0.365	0.065	0.430
26	1.0		0.814	0.066	0.880	0.281	0.174	0.455	0.502	0.000	0.502	0.508	0.025	0.533
27	1.0		1.045	0.113	1.158	0.952	0.000	0.952	0.760	0.000	0.760	0.720	0.044	0.764
28	1.0		1.011	0.075	1.086	1.098	0.000	1.098	0.740	0.000	0.740	0.816	0.000	0.816
29		1.6	0.685	0.177	0.862	0.513	0.042	0.555	0.334	0.054	0.388	0.428	0.009	0.437
30		1.6	0.576	0.114	0.690	0.700	0.093	0.793	0.520	0.000	0.520	0.440	0.096	0.536
31		1.6	0.935	0.167	1.102	0.844	0.132	0.976	0.886	0.005	0.891	0.792	0.000	0.792
32		1.6	1.378	0.219	1.597	1.152	0.132	1.284	1.020	0.000	1.020	1.062	0.019	1.081

mined in the water extract as such. They are arbitrarily calculated to sodium carbonate in order to compare them with the percentages of sodium salts added.

Table 3 contains data corresponding in detail in tables 1 and 2 with the exception that the results are all expressed on the basis of percentage of recovery of the salts calculated from amount of salts added for all concentrations of each soil.

Table 4 represents the equilibrium that is established at the different periods between the sodium carbonate and sodium bicarbonate salts. The data are obtained by calculating the carbonate fraction of the recovery to per cent of total recovery.

Table 5 represents the data for the recovery from that portion of the first series which was taken out at the initial mixing and kept in the air-dry condition throughout the period of the first series. It corresponds in detail to table 1.

EXPLANATION OF THE CHARTS

In order to bring out more clearly the results given in tables 1 and 2 for the four soils, charts were prepared which illustrate graphically the data.

Figures 1-4 include all the data given in tables 1 and 2. The reader must bear in mind that in all cases the sodium bicarbonate curve is expressed in terms of the equivalent of sodium carbonate. As an explanation it may be said that the numerical ratio of sodium carbonate to sodium bicarbonate is 0.63 to 1.0. The figures include curves showing the per cent of each salt recovered after definite periods of contact as indicated by the chart. The total salt recovery is also illustrated by a curve. This curve is the sum of the sodium carbonate recovered together with the sodium bicarbonate. The sodium bicarbonate is, however, calculated to the equivalent of sodium carbonate. The break in the curve, between the dates July 26 and August 10, represents the time of preparation of the soils and the extra addition of salts for the second series. These soils were allowed to stand for an additional short period before sampling in order to establish partial equilibrium. The first sampling of the second series was made on September 15, 1921.

Figures 5 and 6 show the amounts of salts added in both series 1 and 2 for all soils; the amount of each salt recovered at the final period of analysis; and lastly the total salt recovery for each soil. These figures show by means of graphs the final results of the entire time of contact and may well be called summary of graphs which represent the total salt recovery for each individual soil for the entire period of the experiment.

DISCUSSION

In discussing tables 1-4 the period from December 23, 1920 to July 26, 1921 will be referred to as the first series; from August 10, 1921 to October 19, 1922 as the second series. The first four numbers for each soil will be referred to as the carbonate group or additions, and the last four as the bicarbonate. The

TABLE 3
Ratio of salts recovered to salts added in terms of carbonate

POT NUMBER	FIRST SERIES						SECOND SERIES			
	Portion maintained at optimum moisture content				Portion left air dry		Maintained at optimum moisture content			
	Dec. 23, 1920	Jan. 3, 1921	Feb. 25, 1921	July 26, 1921	Nov. 2, 1921	Feb. 7, 1923	Sept. 15, 1921	Dec. 12, 1921	June 10, 1922	Oct. 19, 1922
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
<i>Palouse silt loam</i>										
1	73	32	23	12	56	52	33	27	29	32
2	66	39	23	21	56	56	31	34	34	28
3	68	42	28	28	61	58	36	25	23	22
4	74	40	38	32	66	62	35	39	40	32
5	74	44	26	12	78	76	32	27	30	22
6	91	45	27	21	82	81	17	21	29	26
7	91	42	27	21	82	80		36	32	26
8	85	35	42	25	80	79		33	33	28
<i>Caldwell silt loam subsoil</i>										
9	86	61	50	35			49	45	31	29
10	61	51	38	31	47	47	38	52	35	34
11	76	41	36	26			38	33	26	22
12	65	44	31	23	55	55	36	29	21	17
13	85	61	53	37	63	61	37	26	29	26
14	94	47	47	31	71	67	52	36	41	23
15	90	40	38	32	61	57	51	48	43	40
16	86	55	45	41	73	73	64	51	43	42
<i>Boise silt loam containing natural alkali chlorides and sulfates</i>										
17	56	35	28	17	55	67	42	44	28	24
18	43	32	18	20	37	47	41	38	29	25
19	62	37	29	19	45	43	43	40	31	34
20	62	42	42	30	51	48	52	44	33	37
21	93	36	34	15	58	66	43	28	26	22
22	91	30	20	19	68	56	49	39	27	25
23	80	34	28	22	61	53	57	46	33	36
24	78	35	36	31	63	36	47	40	33	35
<i>Boise silt loam free from alkali chlorides and sulfates</i>										
25	86	65	60	46	65	48	50	53	36	34
26	51	60	50	36	62	43	59	30	33	35
27	71	46	56	34	54	55	58	47	38	38
28	66	50	46	38	56	57	43	44	29	32
29	96	78	60	48	73	66	69	44	31	35
30	85	57	48	39	75	71	46	53	34	35
31	83	44	46	37	73	65	55	49	44	37
32	82	44	52	41	71	68	63	51	40	43

TABLE 4

Ratio of normal carbonate to total carbonate equivalent in recovery

POT NUMBER	FIRST SERIES						SECOND SERIES			
	Portion kept at optimum moisture				Air-dry portion					
	Dec. 23, 1920	Jan. 3, 1921	Feb. 25, 1921	July 26, 1921	Nov. 2, 1921	Feb. 7, 1923	Sept. 15, 1921	Dec. 12, 1921	June 10, 1922	Oct. 19, 1922
	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent
<i>Palouse silt loam</i>										
1			21.7				85.0	68.5	53.3	42.2
2	25.6	32.6	22.6	11.5	7.5	15.4	77.0	62.4	53.0	68.7
3	51.4	54.0	59.2	49.2	28.2	39.5	79.2	92.2	98.0	94.6
4	63.6	69.5	51.1	68.2	46.8	56.5	78.3	76.2	64.6	86.4
5		18.0	9.1				81.5	71.8	45.7	61.4
6		36.8	50.6	16.1			18.4	65.8	58.0	44.5
7		54.2	55.6	34.7				80.8	67.1	78.9
8	1.5	71.1	73.2	62.3		2.0		83.1	77.2	82.0
<i>Caldwell silt loam subsoil</i>										
9	28.8	40.2	58.8	54.0			81.0	86.0	94.3	94.8
10	60.6	63.4	75.6	79.4	57.0	48.8	82.0	91.4	93.0	100.0
11	84.0	90.3	78.5	77.8			92.0	100.0	88.2	100.0
12	86.6	98.0	83.0	86.0	73.0	72.0	91.4	94.1	89.4	96.7
13		53.8	53.6	51.2	3.4		76.6	78.4	87.5	94.0
14	8.9	70.0	77.3	69.7	9.2	4.1	87.5	88.4	70.8	94.5
15	11.4	97.5	82.5	79.1	14.2	2.1	84.2	92.0	100.0	98.0
16	10.3	94.0	80.6	89.2	3.4	7.0	89.4	95.5	97.0	94.5
<i>Boise silt loam containing natural alkali chlorides and sulfates</i>										
17	28.8	22.2	34.3	23.2	39.0	39.5	92.0	88.8	91.0	77.2
18	57.6	50.6	54.2	48.0	50.0	50.0	81.7	85.5	84.5	100.0
19	100.0	72.8	90.5	76.4	67.1	67.0	97.7	90.0	100.0	94.6
20	92.8	98.5	84.0	78.3	76.8	72.0	100.0	92.6	100.0	90.0
21		22.0	70.0	13.1		8.5	85.7	82.4	85.0	80.0
22		40.5	71.5	60.0		3.1	85.3	78.0	98.0	86.5
23	2.5	73.3	72.4	72.8	2.6	6.4	80.5	88.6	100.0	86.6
24	7.1	98.0	97.4	74.4	1.7	44.2	94.2	98.6	100.0	94.0
<i>Boise silt loam free from alkali chlorides and sulfates</i>										
25	67.3	50.6	62.2	66.4	56.8	56.0	87.8	69.2	100.0	85.0
26	40.5	83.4	97.0	74.6	62.2	73.5	92.3	61.8	100.0	94.3
27	90.0	93.5	83.0	77.0	78.2	70.0	90.1	100.0	100.0	94.0
28	99.0	97.5	94.0	88.1	71.1	73.4	93.3	100.0	100.0	100.0
29	19.6	53.3	61.5	70.7	17.9	14.5	79.4	90.5	86.2	98.0
30	19.4	79.2	87.2	78.8	12.9	9.5	83.5	88.4	100.0	82.2
31	19.9	88.8	77.2	87.7	10.3	13.1	84.6	86.4	99.5	100.0
32	8.4	97.0	83.2	89.6	5.6	10.6	86.4	90.0	100.0	98.4

additions and recoveries are expressed as grams per hundred grams of anhydrous soil. In inspecting the data in the tables the reader is urged to consider the general trend of results rather than the individual differences between recoveries of the salts that may appear from time to time. The difficulties encountered in obtaining thorough distribution of added salts as well as uniform samples of alkali soils is well known to all who have had experience in alkali investigations.

Palouse silt loam

A critical review of the data dealing with the Palouse silt loam soil shows the large amount of salts that are retained in the soil even when analyzed immediately after mixing the dry salts with the air-dry soil. The percentage of recovery in a water extract of this soil is slightly higher with the bicarbonate than the carbonate salts. It is to be noted that the actual amount of salts recovered with the various concentrations are, within relatively narrow limits proportionate to the amount of salts added.

The rapid change of carbonate salts to bicarbonate is shown by the fact that in the determination made immediately after mixing the salts and soil, considerable of the sodium carbonate is found changed to the bicarbonate. This is contrary to the action of the sodium bicarbonate additions at this time, for only in the heaviest addition of sodium bicarbonate is the normal carbonate found and in this case the amount is insignificant.

The second determination was made on January 3, 1921, or ten days after the salts had been mixed with the soil. During this period they had been kept in a moist condition. At this time the amount of salt retained by the soil had greatly increased, in fact it was practically twice the amount held by the soil when the first sample was taken. In the carbonate additions the carbonate recoveries for two of the concentrations were slightly greater at this period than the recoveries secured immediately after mixing the salts and air dry soil. It was observed that the smallest concentration of sodium carbonate (0.25 gm.) did not yield any recoverable salts as carbonate but had evidently changed into the bicarbonate since some bicarbonate was found in the water extract. This is also true for the first sampling.

In the bicarbonate additions a noticeable change has taken place in the equilibrium of the bicarbonates and carbonates in the soil for there is a large amount of bicarbonate salts changed into carbonates and are recovered as such in the soil extract, the proportion in fact being greater than the actual amounts of carbonate salts recovered from the corresponding carbonate additions.

On February 25, the total recovery of salts continues to fall in all cases except treatment number 8. There are slight rearrangements of the equilibrium of the salts in both additions at this period.

The final determination in this series made July 26, 1921 shows a continued decrease in total recovery in every case. This decrease, however, is very small as compared with the first two periods, the curve being almost a straight line

as shown in figure 1. It is evident that the decrease is greater in the lower concentrations resulting in a smaller recovery of the salts in the lower additions. This soil shows the power of retaining a smaller percentage of the higher than the lower additions of salts. This does not mean that the actual amount of salts retained by the soils receiving the largest additions is less than with the smaller additions. On the contrary, almost five times as much salt is retained by the soil with the greatest addition.

In this series, the per cent of the recovered salts appearing as normal carbonates generally increases with the amount of salts added throughout the series. However, this increase is not in the same ratio as that of the salts added.

The second series, table 2, shows the effect of adding an additional one per cent of sodium carbonate to the sodium carbonate series and an equivalent amount of sodium bicarbonate to the bicarbonate series. The additions were made on August 10, 1921, and moisture was added to the soil at this time. It must be remembered that the total additions of salts to this soil now are 1.25, 1.5, 2.0 and 2.5 gm. of carbonate per 100 gm. of anhydrous soil and their equivalents of sodium bicarbonate. In comparing subsequent recoveries, however, it is justifiable to consider the sum of the amount recovered on July 26, and that added on August 10, as the initial recoverable salt content for the second series. Considering this amount of salt as the basis for recovery we find a large decrease in recovery at the time of the first determination, which was made on September 15, 1921. It is also evident that the ratio of normal carbonate to the total recovery has become more uniform for all additions in both carbonate and bicarbonate groups.

In the second series, an inspection of table 2 and figure 1 shows that equilibrium has practically been established in the Palouse soil for all added concentrations at the time of the first sampling. This is only thirty-five days after the second additions were made to the soil. The last sampling, made over a year later than the initial one, shows only a very slight downward trend. The intermediate determinations show slight fluctuations, some indicating more recovery of salts than others. This is distinctly seen when the graphs in figure 1 are examined. Not much stress can be laid on these fluctuations for it may be due for the most part to differences in sampling these soils. It should be stated here that all concentrations of alkali used on the Palouse soil, especially in the second series resulted in a highly deflocculated soil. The soil was extremely sticky and showed all the appearances of a poor physical condition which is typical with an excess of black alkali.

It is to be observed that in all the highest additions of salts there is a proportionately higher percentage recovery than in the lowest additions. This in turn means that there is proportionately less retention of salts in the highest additions. But it must not be overlooked when commenting on these two facts, that the soil seems to possess a cumulative action in absorbing or retaining the salts. Taking the lowest addition, 0.25 gm., and comparing it with the highest addition, 1.5 gm., only 12 per cent is recovered in the first series

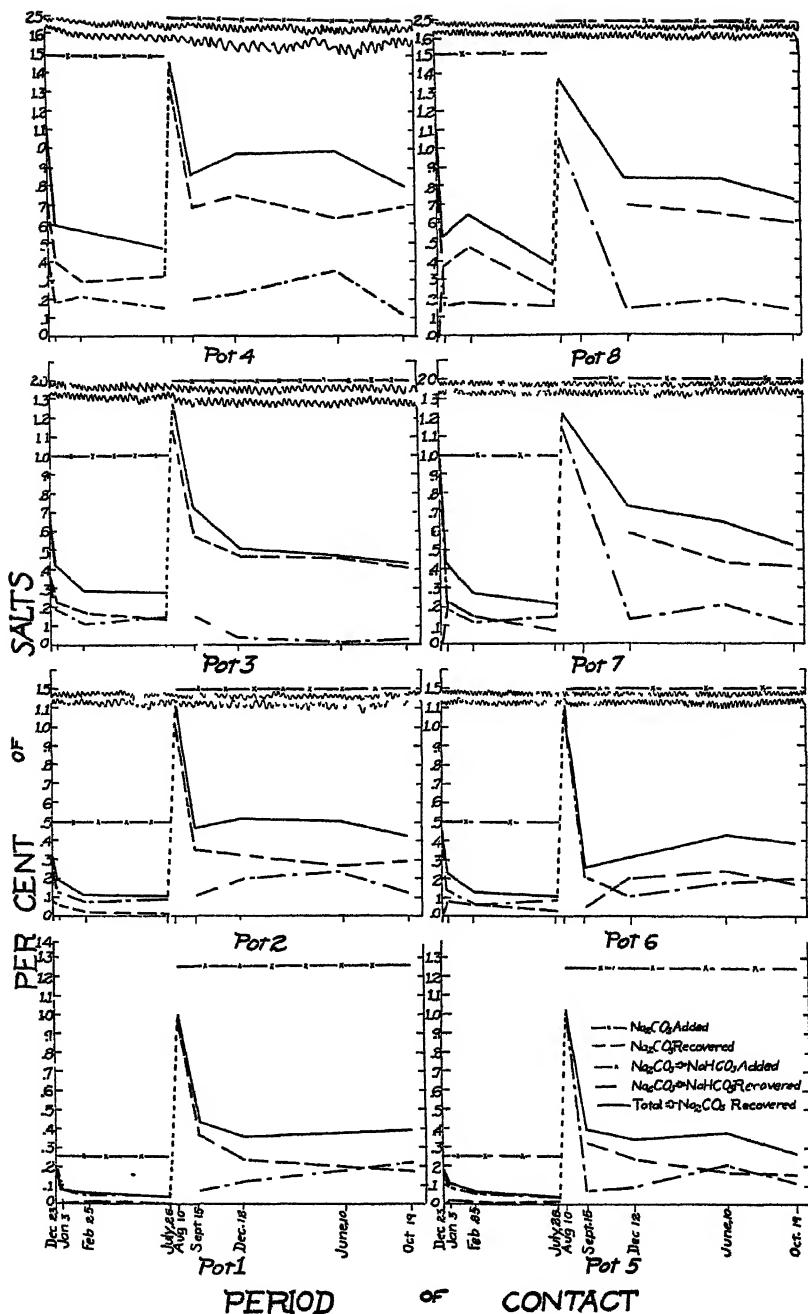


FIG. 1. CURVES REPRESENTING SODIUM CARBONATE AND SODIUM BICARBONATE ADDED TO AND RECOVERED FROM PALOUSE SILT LOAM, WHEN KEPT AT A MOISTURE CONTENT OF 15 TO 20 PER CENT

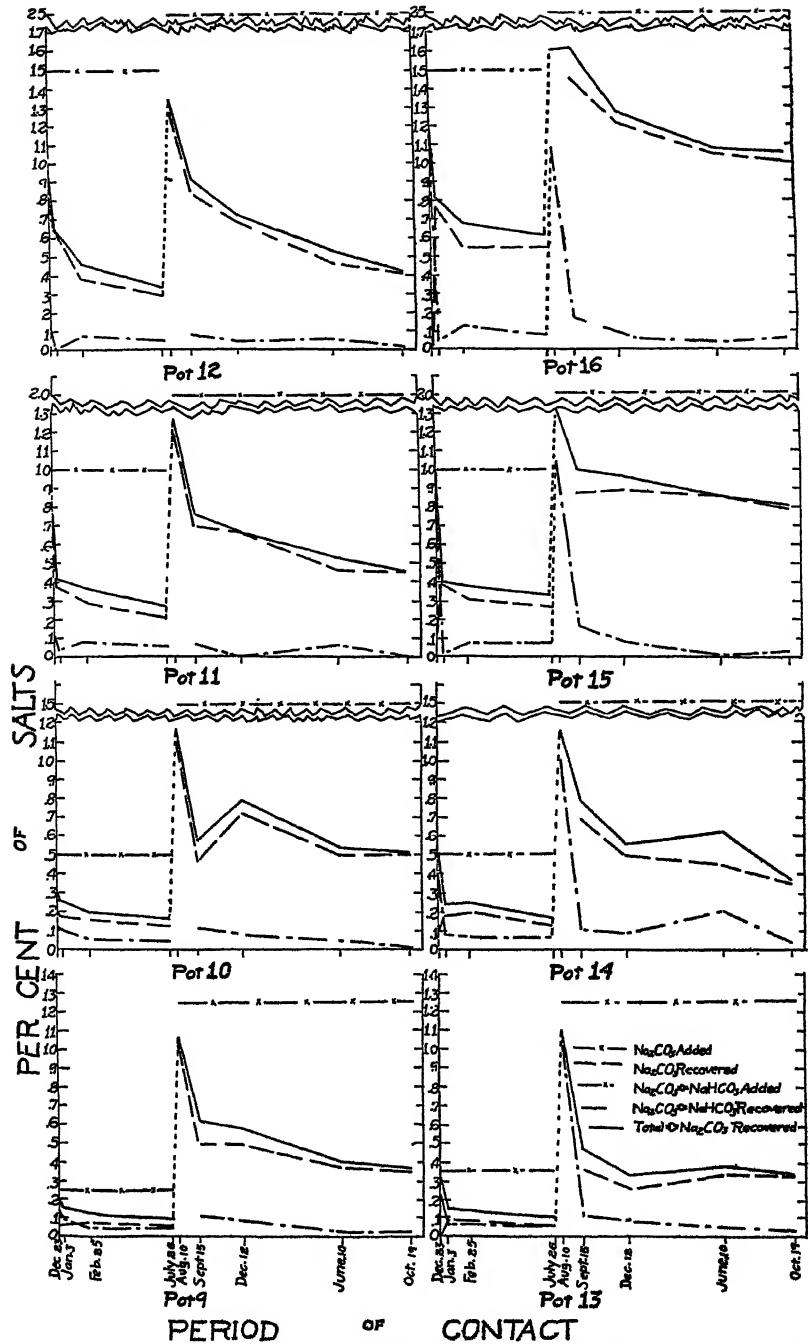


FIG. 2. CURVES REPRESENTING SODIUM CARBONATE AND SODIUM BICARBONATE ADDED TO AND RECOVERED FROM CALDWELL SILT LOAM SUBSOIL, WHEN KEPT AT A MOISTURE CONTENT OF 15 TO 20 PER CENT

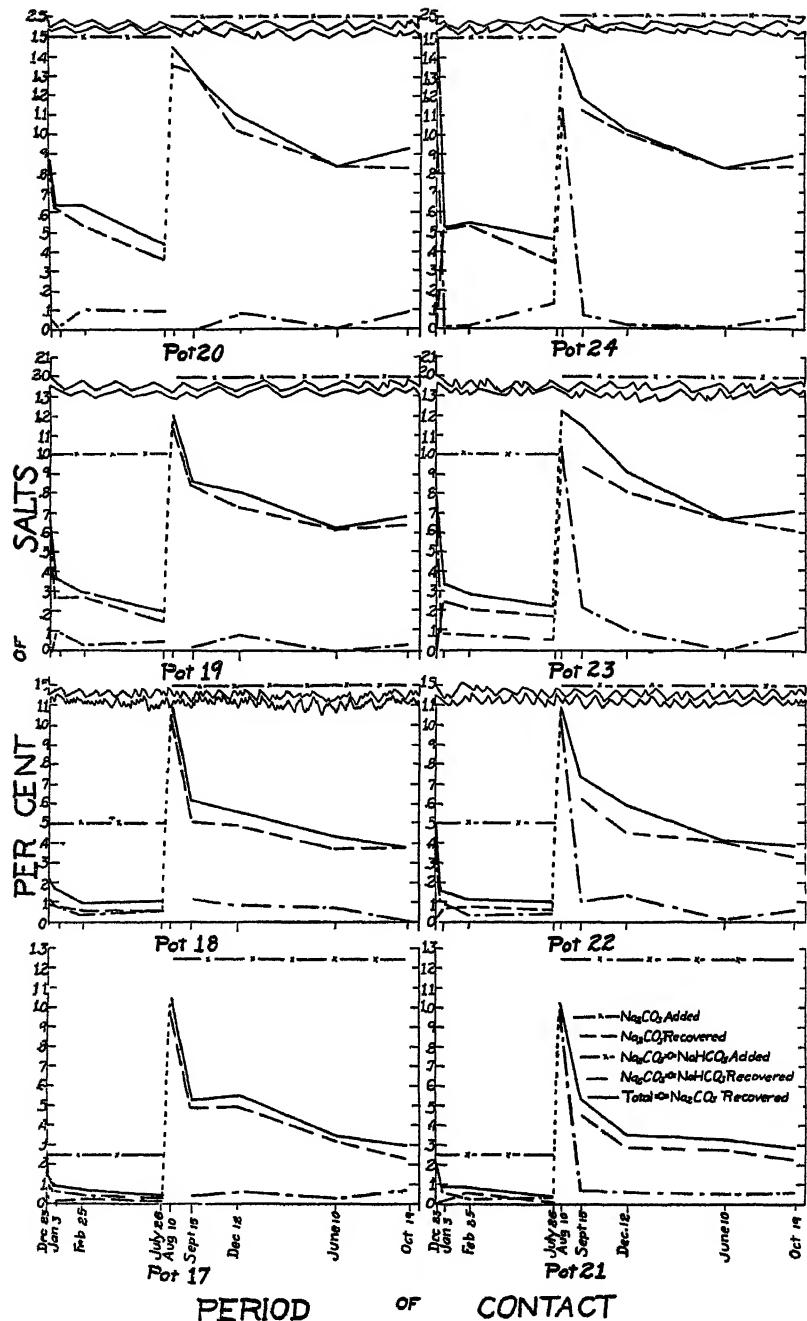


FIG. 3. CURVES REPRESENTING SODIUM CARBONATE AND SODIUM BICARBONATE ADDED TO AND RECOVERED FROM BOISE SILT LOAM CONTAINING NATURAL ALKALI CHLORIDES AND SULFATES, WHEN KEPT AT A MOISTURE CONTENT OF 15 TO 20 PER CENT

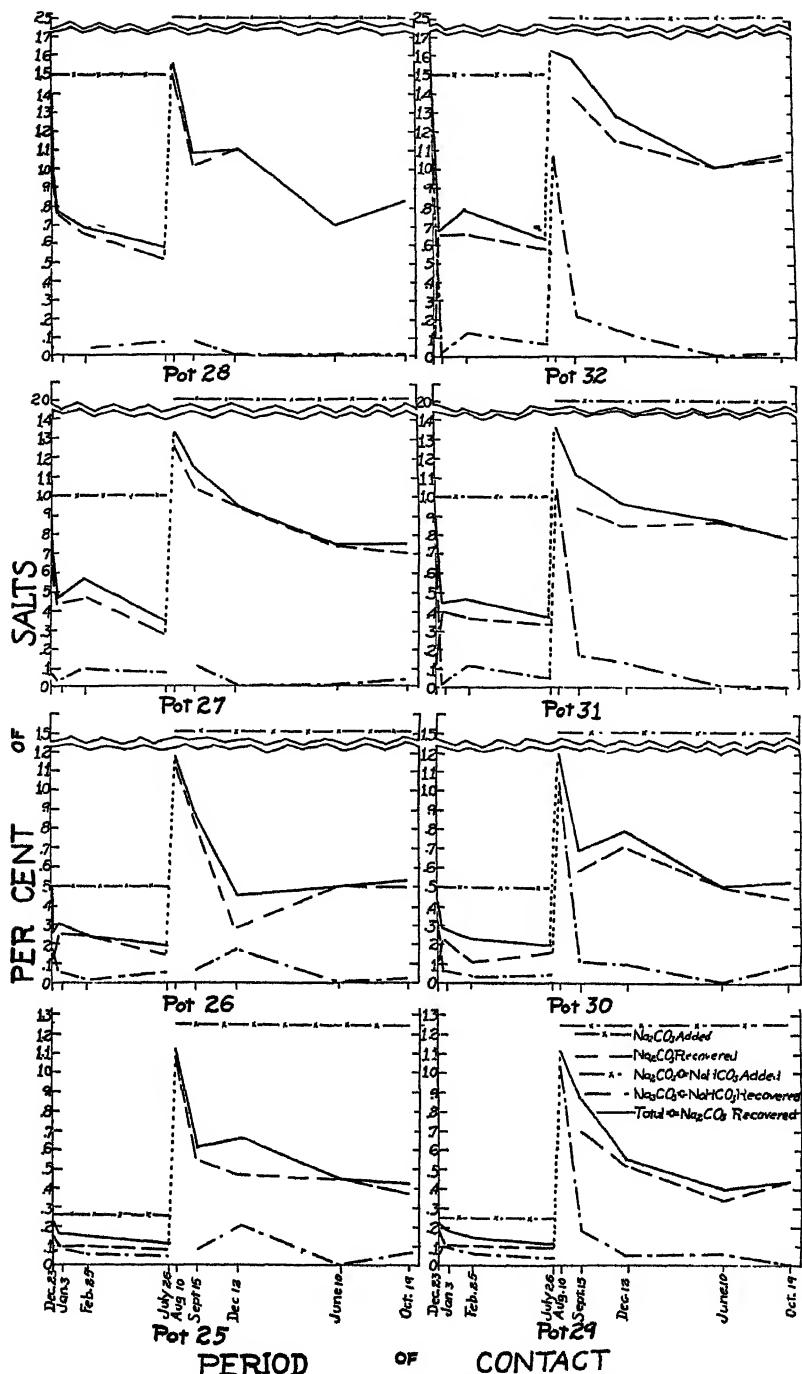


FIG. 4. CURVES REPRESENTING SODIUM CARBONATE AND SODIUM BICARBONATE ADDED TO AND RECOVERED FROM BOISE SILT LOAM FREE FROM ALKALI CHLORIDES AND SULFATES, WHEN KEPT AT A MOISTURE CONTENT OF 15 TO 20 PER CENT

from the lowest addition. With the highest addition 32 per cent is recovered. The percentage absorption is less with the highest addition but when actual amounts are considered we see that the amount of salts retained by the soil in the highest addition is much greater than with the lowest addition. With greater applications, this soil shows the power of increased actual retention or absorption.

In the second series the percentage of retention for the highest and lowest addition is equal at the end of the period, viz., 68 per cent for each treatment, while the actual amount of retention is 1.7 and 0.86 gm., respectively per 100 gm. of anhydrous soil.

It is noted that throughout this series we find a large recovery of normal carbonate in all concentrations. This is in accord with our earlier findings that a larger proportion of the normal carbonate is recovered in the heavier additions.

It is observed that this soil has the power of producing a certain amount of bicarbonate which is not increased with larger additions of salts. In the lowest additions of normal carbonate, it is all changed to bicarbonate. With higher additions the amount found does not exceed a definite level for both series. In the small additions, however, the level rises at once in the second series to the same level as the hither additions and remains there throughout the period.

In the bicarbonate series, we find the salt recovered primarily as such until the amount present exceeds the level found in the carbonate series. All higher additions which come above this general level are changed to normal carbonate. Figure 1 clearly illustrates this point.

In a study of table 3 we note that for the first determination December 23, 1920, all percentage recoveries are high but fairly uniform for all additions. As time goes on, there appears a divergence in percentage recovery between the lower and higher additions. The highest addition in the carbonate series gives a recovery two and one-half times that of the lowest, and in the bicarbonate additions the final recovery is twice as great for the highest additions.

In the second series there are marked irregularities in the per cent recovered. At the end of the period there is, however, a uniformly higher recovery than is found at the end of the first series. This difference is greatest in the lower concentration, the final recovery in the higher concentrations in the second series being surprisingly near that of the first.

The Caldwell silt loam subsoil

Since a detailed discussion has been given for the Palouse silt loam soil it will not be repeated here but only the characteristic differences will be discussed for each of the three remaining soils. The Caldwell soil shows quite a similar recovery to the Palouse soil of both salts in the first analysis of the first series. The remaining three samplings of this series show a much higher recovery than in the Palouse soil.

In the normal carbonate additions of the first series the percentage of recovered salts is smaller for the larger than the smaller additions. This is true for both first and second series and is the reverse of the condition found on the Palouse soil. The bicarbonate additions to the Caldwell soil show the same type of recovery curve as the Palouse soil, differing only in that the Caldwell soil gives higher percentage recoveries in both series. The total carbonate recovery from the normal carbonate additions is lower throughout than that from the corresponding additions of the bicarbonate group.

From table 4 we see that the Caldwell soil shows little power of changing added carbonate salts to bicarbonate since practically all of the recovered salt from the carbonate additions is in the form of normal carbonate. On the other hand it does show marked activity in changing the bicarbonate additions to normal carbonate for by far the greater per cent of the added bicarbonate salt is recovered as the normal carbonate. The final percentage recoveries for both the normal carbonate and bicarbonate are very similar, ranging from 94 per cent to 100 per cent recovery as normal carbonate regardless of the salts added.

Boise silt loam

The Boise silt loam soil containing natural alkali salts, in the form of chlorides and sulfates, shows a lower initial recovery in the carbonate group than either the Palouse or Caldwell silt loam soils. The bicarbonate group, however, gives very nearly the same recovery as that of the Palouse soil. In the second and following determinations in the first series the relative recoveries are very nearly the same as those of the Palouse soil. The carbonate fraction of the total is very nearly the same as that for the Caldwell soils. The recoveries in the second series are high in the first determination, being almost equal to the results found in the Caldwell soil. The final recovery has dropped to the level of the Palouse soil.

In the alkali-free sample of the Boise silt loam we find the total recovery in the first determination about the same as the first two described soils, but in the succeeding determinations there is a smaller decrease in recovery than in any other soil giving us a larger recovery at the end of the first period than any other soil used in the experiment. In the second series the recovery is the largest throughout the period. This soil shows the weakest retentive power of any of the soils studied. It will be noted in the final determination of the second series that the percentage of recovery is less than the final recovery in the first series even though 1 gm. additional salt was added. The proportion of normal carbonate present in the first determination in the first series is the highest of all. This is especially noticeable in the bicarbonate group.

CARBONATE EQUILIBRIUM IN THE SOILS KEPT AIR-DRY

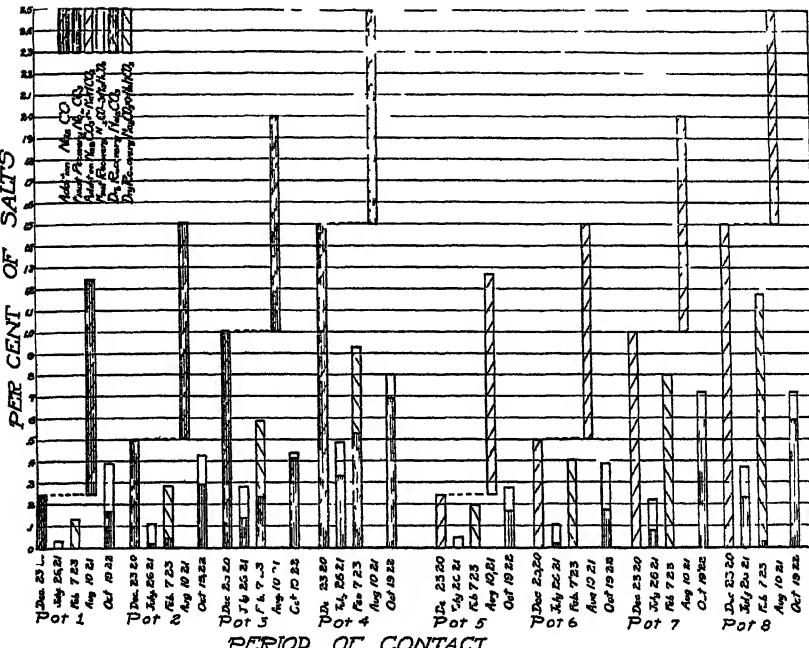
At the beginning of the experiment when the soils were mixed with the salts in an air-dry condition a portion of the soil containing each of the salt

TABLE 5

Carbonates added and recovered from soils maintained in an air-dry condition. First series

POT NUMBER	SALTS ADDED PER 100 GM. ANHYDROUS SOIL		SALTS RECOVERED IN WATER EXTRACT PER 100 GRAMS OF ANHYDROUS SOIL								
			December 23, 1920			November 2, 1921			February 7, 1923		
	Na ₂ CO ₃	NaHCO ₃	Na ₂ CO ₃	NaHCO ₃ expressed as Na ₂ CO ₃	Total Na ₂ CO ₃ equivalent	Na ₂ CO ₃	NaHCO ₃ expressed as Na ₂ CO ₃	Total Na ₂ CO ₃ equivalent	Na ₂ CO ₃	NaHCO ₃ expressed as Na ₂ CO ₃	Total Na ₂ CO ₃ equivalent
	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.
<i>Palouse silt loam</i>											
1	0.25		0.000	0.183	0.183	0.000	0.140	0.140	0.000	0.132	0.132
2	0.5		0.083	0.241	0.324	0.021	0.266	0.288	0.043	0.236	0.279
3	1.0		0.353	0.334	0.687	0.174	0.442	0.616	0.230	0.351	0.581
4	1.5		0.706	0.406	1.110	0.468	0.532	1.000	0.523	0.398	0.921
5		0.4	0.000	0.180	0.180	0.000	0.197	0.197	0.000	0.190	0.190
6		0.8	0.000	0.456	0.456	0.000	0.414	0.414	0.000	0.405	0.405
7		1.6	0.000	0.915	0.915	0.000	0.820	0.820	0.000	0.801	0.801
8		2.4	0.02	1.250	1.270	0.000	1.200	1.200	0.024	1.172	1.196
<i>Caldwell silt loam subsoil</i>											
9	0.25		0.062	0.153	0.215	*					
10	0.5		0.187	0.122	0.309	0.136	0.102	0.239	0.115	0.121	0.236
11	1.0		0.644	0.122	0.766	*					
12	1.5		0.852	0.132	0.984	0.610	0.226	0.936	0.592	0.232	0.824
13		0.4	0.000	0.213	0.213	0.005	0.153	0.158	0.000	0.153	0.153
14		0.8	0.042	0.427	0.469	0.032	0.322	0.355	0.014	0.324	0.338
15		1.6	0.104	1.065	1.169	0.087	0.523	0.610	0.120	0.458	0.578
16		2.4	0.124	1.180	1.304	0.038	1.160	1.100	0.077	1.021	1.098
<i>Boise silt loam containing natural alkali, chlorides and sulfates</i>											
17	0.25		0.041	0.101	0.142	0.054	0.083	0.138	0.067	0.102	0.169
18	0.5		0.124	0.091	0.215	0.092	0.093	0.186	0.120	0.118	0.238
19	1.0		0.623	0.000	0.623	0.305	0.149	0.454	0.288	0.142	0.430
20	1.5		0.873	0.061	0.934	0.392	0.178	0.770	0.521	0.204	0.725
21		0.4	0.000	0.233	0.233	0.000	0.146	0.146	0.014	0.151	0.165
22		0.8	0.000	0.456	0.456	0.000	0.341	0.341	0.009	0.276	0.285
23		1.6	0.02	0.781	0.807	0.016	0.595	0.611	0.034	0.500	0.534
24		2.4	0.083	1.078	1.161	0.016	0.940	0.956	0.240	0.302	0.542
<i>Boise silt loam free from alkali chlorides and sulfates</i>											
25	0.25		0.146	0.071	0.214	0.092	0.070	0.163	0.067	0.053	0.120
26	0.5		0.104	0.151	0.257	0.195	0.118	0.313	0.158	0.061	0.219
27	1.0		0.644	0.071	0.715	0.429	0.120	0.549	0.389	0.167	0.556
28	1.5		0.996	0.010	1.006	0.598	0.241	0.839	0.628	0.228	0.856
29		0.4	0.047	0.193	0.240	0.032	0.149	0.182	0.024	0.141	0.165
30		0.8	0.083	0.344	0.427	0.049	0.330	0.379	0.034	0.325	0.359
31		1.6	0.166	0.666	0.834	0.076	0.662	0.738	0.086	0.572	0.658
32		2.4	0.104	1.135	1.239	0.060	1.020	1.080	0.101	0.927	1.028

* Lost.



NOTE TREATMENTS AND RESPECTIVE SALT RECOVERY AT THE END OF EACH

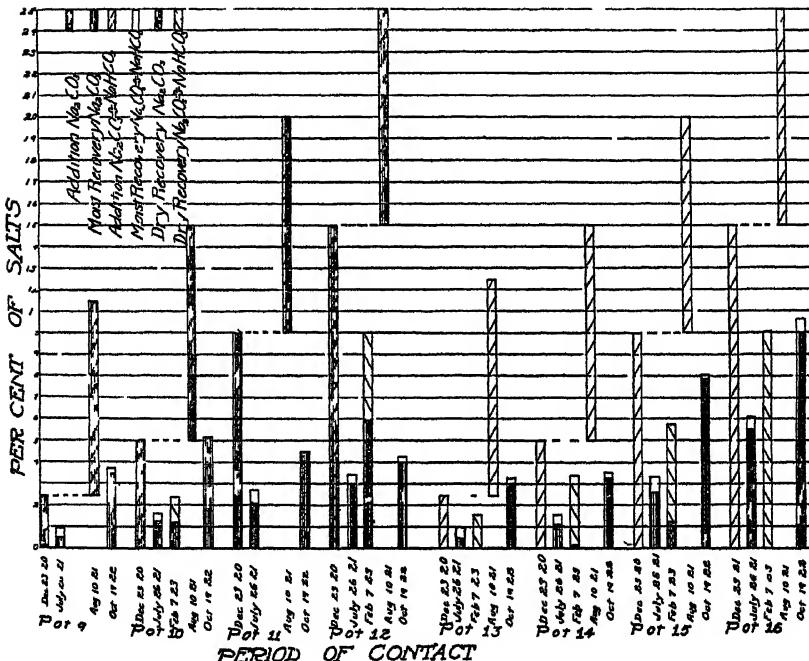
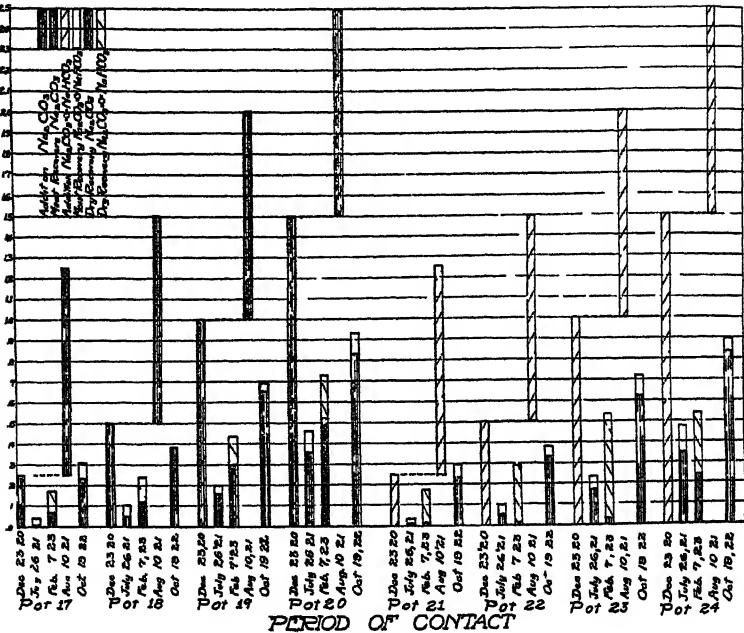


FIG. 5. DIAGRAM REPRESENTING SUCCESSIVE SODIUM CARBONATE AND SODIUM BICARBONATE ADDITIONS TO THE

PER CENT OF SALTS



PER CENT OF SALTS

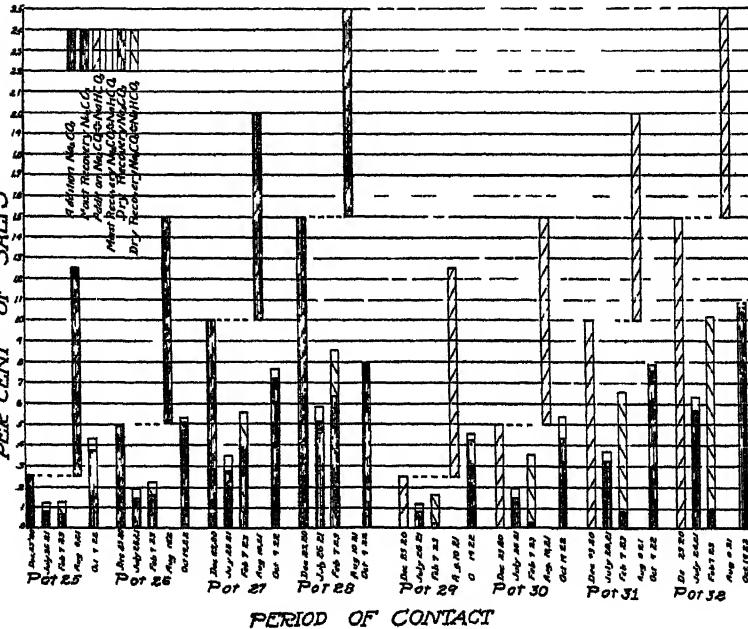


Fig. 6. DIAGRAM REPRESENTING SUCCESSIVE SODIUM CARBONATE AND SODIUM BICARBONATE TREATMENTS AND RESPECTIVE SALT RECOVERY AT THE END OF EACH SERIES

concentrations was placed in small wide-mouth bottles and set aside in the greenhouse. These soils were kept in an air-dry condition throughout the entire period of the experiment in order to observe the behavior of the carbonate and bicarbonate salts in air dry soils. The soil was analyzed December 23, 1920, immediately after mixing. The results are the same as given for the moist soils for that date. Additional determinations were made on November 2, 1921, approximately eleven months after mixing, and on February 7, 1923, approximately twenty-six months after the beginning of the experiment. The results are given in tables 3, 4 and 5.

While a comparison of the recoveries made eleven and twenty-six months after mixing shows variation in amounts recovered, a general similarity exists for all four soils in that the determinations made eleven months after mixing are considerably lower than the results obtained at the beginning of the experiment. The recoveries obtained twenty-six months after beginning the experiment, or fourteen months after the second sampling, show that very slight changes have resulted, and only a slight reduction in total recovery is noted.

In pots 24 and 26 there is noted a larger decrease in the amount of recoverable salt at the last period of sampling. These discrepancies are due to the fact that water leaked into these bottles from the greenhouse roof and the soils became moist before it was noticed. They were allowed to dry out again, but a change had taken place in the equilibrium as noted in the results.

In the dry condition, it was noticed that the soil did not change the bicarbonate salts into carbonates but the soils showed the same relative power to change carbonates into bicarbonates that was observed with these same soils when maintained in a moist condition. In pot 24 the high recovery of normal carbonate from the bicarbonate addition was due to the accidental contamination by water as previously mentioned.

In all soils the total recoveries of the bicarbonate additions are greater than the normal carbonate.

In the Boise silt loam containing natural alkali we find a higher percentage of recovery with the smallest addition than with the largest additions, both with the carbonate and bicarbonate. This is contrary to the results obtained on the other three soils.

THE ABSORPTION PHENOMENA OF SODIUM CARBONATE IN SOILS

It has long been known that some of the additions of sodium carbonate salts could not be recovered in a water extract of the soils. In other words, each soil has a capacity for retaining a certain portion of the added salt. The amount of sodium carbonate recoverable is an individual characteristic for each soil. Clays and soils high in organic matter are known to absorb more carbonate salts than sands.

The additions of carbonate produce a distinct physical and chemical effect on soils. In small amounts sodium carbonate has proved a stimulant to the growth of certain crops on many soils. In the alkali tolerance studies carried

on at this station the writers have repeatedly found stimulation as shown by increased yields of crops treated with small dilutions of sodium carbonate over the pots receiving no treatments. Other investigators have reported similar experiences.

In the present investigation it will be noted that four treatments were made to the first series, varying in concentration from 0.25 to 1.5 per cent sodium carbonate. It was found that the percentage of retention or absorption varied with the minimum and maximum additions of carbonates, for the soils in the experiment, some of the soils showing a smaller percentage retention with the minimum than with the maximum additions, and vice versa. This is only to be expected for it demonstrates the individual characteristic of each soil towards absorption. It must be borne in mind that the larger additions all show a much greater absorption in the soil, regardless of the percentage of recovery. When one per cent additional sodium carbonate was added to the soils in the second series, we had concentrations of 1.25 per cent as the minimum and 2.5 per cent as the maximum. These concentrations were sufficient to materially change the physical condition of the soil. It must be admitted that these concentrations of the second series are all far in excess of sodium carbonate which can be tolerated by crops. In considering the recovery of salts from these soils, we find that the addition of the one per cent sodium carbonate to soils in the first series had reached an equilibrium as indicated by chemical analysis of the water extract and to which the maximum addition of 1.5 per cent sodium carbonate was thought to show the maximum absorption showed instead an added capacity of absorbing sodium carbonate. One of the soils, e.g. the Palouse silt loam, attained almost a similar equilibrium at the first sampling as was found thirteen months later. The remaining soils all showed a decided decrease in salts recovered and a corresponding increase in salts absorbed.

It may seem somewhat strange that soils show an added capacity for absorption or retention of carbonate salts after the first equilibrium had taken place in the first series. A tentative explanation is offered here.

As early as 1888 Van Bemmelen (15) in studies on soil absorption concluded that the chief absorptive power of a soil is due to the colloidal oxides and silicates present in it. He stated that the soil contains colloids, colloidal silicates, iron oxide, silicic acid and humus substances, all of which bring about these reactions and tend to change the equilibrium, thereby causing considerable absorption in soils.

It is noted in this work that more carbonates are absorbed from concentrated than from dilute solutions. Even if the concentrations were very low, e.g. 0.25 per cent, the entire salt was not removed by the soil. This fact has been mentioned frequently in the literature in discussing absorption of salts by soils.

It is quite possible that sodium carbonate when added to soils reacts with the constituents already present in the soil and is therefore, removed from the

soil solution as carbonates or changed into other forms. One such possible reaction is that between sodium carbonate and the silicates of the soil. MacIntire, Willis, and Hardy (13) have demonstrated such reaction when magnesium carbonate is added to soils. We have, therefore, a change of carbonate to silicates with a loss of carbon dioxide.

It is evident then that an analysis of a water extract of soils to which salts were added would not show a total recovery of salts as CO_3 and HCO_3 . Here it is seen that this unrecovered portion would be considered as absorbed by the soil, but this absorption would on the other hand not be due entirely to the sodium carbonate removed as such by the soil, but would be partly due to the resultant of the interreactions of silicates and carbonates. Such reactions have been shown to take place easily.

Chief among the investigations describing the above cited reactions is the classic work of Lemberg (9), who demonstrated that an exchange of bases can take place between a silicate and salt solution; by the addition of a free base to the silicate from an alkaline solution or by the addition of the entire salt. Sullivan (14, p. 5-36) has developed additional data on the base exchange theory in regard to salts and silicates. He states, "Where the solution is alkaline in reaction, containing a soluble hydroxide dissolved as such or a salt made up of a strong base and a weak acid (as the carbonates, silicates and phosphates of sodium and potassium) which is hydrolyzed by water with resulting formation of free alkali; its behavior with clay, soils, etc., is due largely to the presence of colloid silica or aluminum silicate, and consists primarily in the direct addition of alkali to these solids, without substitution, insoluble silicates or alumino-silicates being found." Armsby (1) has also discussed the nature of absorption of bases by silicates and pointed out that the absorption is in accordance with the law of mass action. He illustrates experimentally the reason that no relation of chemical equivalence existed between the quantity of base taken up and the quantity of any single constituent in the soil. The reason for this was not explained by Way (16) and others when they attempted to use this fact as evidence of a physical surface absorption phenomena rather than a chemical reaction in soil. Henneberg and Stohmann (6) found that the greater the amount of solution of a salt taken with a fixed quantity of soil, the greater was the absorption. In certain cases doubling the amount of solution increased the amount of absorption by one-fifth. E. A. Fisher (3) has assembled and critically discussed the views of several investigators on the absorption phenomena in soils.

Because of the possible reactions which may occur between the soil and an added salt such as sodium carbonate, it is suggested that a part of the additions of sodium carbonate not recoverable in the water extracts may not exist as such in the soil but may have been changed into other forms and may not have been absorbed as sodium carbonate. This conclusion has some support in the fact that the salt additions to the soil gradually come to an equilibrium; very rapidly at first with the more concentrated solutions and then more gradually until only slight changes occur. In the second series with the heavy additions the major equilibrium reactions took place rapidly and varied but slightly during the remaining period of contact. Here it is evident that concentration played a considerable part in the speed with which the general point of equilibrium was reached. It is quite evident that one of the chief factors of equilibrium in soils is the solubility factor of the salts entering into

the reactions but to attempt to fix anything but generalities in the rate of equilibrium reactions in soils would be the utmost folly because of the complexity of the media involved. It appears that the solubility of the silicates in the soils has much to do with the rate of reaction and this in part accounts for the gradual change in equilibrium resulting in a decrease in amount of recoverable salt as time elapses. Slight deviations from time to time might be accounted for by the difficulty of securing uniform samples and by the reversibility of the reactions occurring in the soil.

The three soils are somewhat different in texture. The Palouse silt loam is quite high in organic matter; the Caldwell silt loam subsoil contains considerably more clay than the other two soils; the Boise silt loam borders on a sandy loam. The final recovery of carbonates in general is less with the Caldwell soil containing considerable clay. Very little difference is noted between the other soils. In discussing the bicarbonate recoveries in general it must be said that the reverse of the carbonate series is true.

The entire work tends to show the extreme ability of a soil to establish an equilibrium between added salts even when added in a so-called cumulative manner.

So many factors must be considered in discussing absorption in soils, since soils are so complex and varying in nature that these suggestions on the absorption of carbonates are only offered as tentative explanations. The fact that the recoverable and not added carbonate salts are the criterion for determining toxicity of plants may be partially explained by the fact that the absorbed salts have been changed in part to other forms. Cognizance is taken of the fact that absorption of sodium carbonate *per se* by the finely divided material present in soils may and undoubtedly does take place. This absorption may be classed as mechanical in nature, or purely surface absorption.

SUMMARY

1. Absorption increased rapidly from the initial mixing of salts until a maximum was reached, after which the time of contact had little influence upon the percentage absorption of added salts.

2. After the equilibrium was reached in the first series, additional salts added to these same soils resulted in an equilibrium similar to that established in the first series. A notable feature of the second series of added salts is that the soils responded to these treatments of added carbonates in a manner similar to that of the first series. The soils established an added absorption in a similar degree to that of the first series. How long these soils would show this same capacity for additional absorption can not be stated since these experiments were concluded after two additions of salts.

3. Addition of carbonate salts to soils, immediately showed a portion of the recoverable salts as bicarbonates. The extent of this change depended chiefly upon the individual soil. Bicarbonate additions to moist soils showed recoverable salts determined as normal carbonate after a short period of contact.

4. Within the range of concentrations of salts added, these four soils showed a greater absorption for the greater concentrations of added salt.

5. The four soils were assumed to be widely different at the beginning of the experiment, but at the conclusion, or when equilibrium was established they showed very similar capacities for absorption.

6. Differences of absorption were more noticeable with the four soils when the salts were in contact for short periods indicating that greater absorption takes place when the concentration of salt was the highest.

7. Carbonate and bicarbonate salt treatments to soils maintained in an air-dry condition showed much less absorption than soils maintained at the optimum moisture content. In air-dry soils a part of the carbonates were changed to bicarbonates. Bicarbonate additions were not changed to carbonate in any great degree.

8. It is suggested that a portion of the sodium carbonate, not recovered in the water extract and generally conceded to be absorbed by the soil, is in reality changed into other compounds, which makes it impossible to secure a quantitative recovery.

REFERENCES

- (1) ARMSBY, H. P. 1877 Ueber das Absorptionsvermögen des Bodens für Basen. *In Landw. Versuchs. Stat.*, v. 21, p. 397-405.
- (2) CAMERON, F. K., AND BRIGGS, L. J. 1901 Equilibrium between carbonates and bicarbonates in aqueous solutions. *In U. S. Dept. Agr. Bur. Soils Bul.* 18, "Solution studies of salts occurring in alkali soils," p. 9-24.
- (3) FISHER, E. A. 1922 The phenomena of absorption in soils: A critical discussion of the hypothesis put forward. *In Proc. Farad. Soc.*, v. 17, pt. 2., p. 305-316.
- (4) HARRIS, F. S., AND PITTMAN, D. W. 1918 Soil factors affecting the toxicity of alkali. *In Jour. Agr. Res.*, v. 15, p. 287-319.
- (5) HEADLY, F. B., CURTIS, E. W., AND SCOFIELD, C. S. 1916 Effect on plant growth of sodium salts in the soil. *In Jour. Agr. Res.*, v. 6, p. 856-869.
- (6) HENNEBERG, W., AND STOHMANN, F. 1859 Ueber das Verhalten der Ackererde gegen Lösungen von Ammoniak und Ammoniaksalzen. *In Jour. f. Landw.*, v. 3, p. 25-47.
- (7) KEARNEY, T. H. 1920 The relative absorption by soils of sodium carbonate and sodium chloride. *In Soil Sci.*, v. 9, p. 267-273.
- (8) KEARNEY, T. H., AND CAMERON, F. K. 1902 The effect upon seedling plants of certain components of alkali soils. *In U. S. Dept. Agr. Rpt.* 71, p. 7-60.
- (9) LEMBERG, J. 1870 Ueber einige Umwandlungen findlandischer Feldspathe. *In Ztschr. Dent. Geol. Gesell.*, v. 22, p. 335-372.
- (10) LEMBERG, J. 1872 Ueber die Contactbildungen bei Predazzo. *In Ztschr. Dent. Geol. Gesell.*, v. 28, p. 519-621.
- (11) LEMBERG, J. 1876 Ueber Silicatumwandlungen. *In Ztschr. Dent. Geol. Gesell.*, v. 28, p. 519-621.
- (12) LEMBERG, J. 1877 Ueber Gesteinsumbildungen bei Predazzo und am Monzoni. *In Ztschr. Dent. Geol. Gesell.*, v. 29, 457-510.
- (13) MACINTIRE, W. H., WILLIS, L. G., AND HARDY, J. I. 1914 The non-existence of magnesium carbonate in humid soils. *Tenn. Agr. Exp. Sta. Bul.* 107.
- (14) SULLIVAN, E. C. 1907 The interaction between minerals and water solutions, with special reference to geologic phenomena. *U. S. Geol. Sur. Bul.* 312.

- (15) VAN BEMMELLEN, J. M. 1888 Die Absorptionsverbindungen und das Absorptionsvermögen der Ackererde. *In* Landw. Vers. Stat., v. 35, p. 69-136; also in Du Absorption, pub. by Steenkoff, Dresden.
- (16) WAY, J. THOMAS. 1850. On the power of soils to absorb manure. *In* Jour. Roy. Agr. Soc., England, v. 11, p. 313-379.

THE VARIANT RÔLES OF SOIL AND SUBSOIL IN CALCIUM-MAGNESIUM INTERCHANGE

W. H. MacINTIRE, W. M. SHAW AND J. B. YOUNG

University of Tennessee Agricultural Experiment Station

Received for publication June 1, 1923

INTRODUCTORY

In the expansion of earlier studies upon the activities of the different oxides and carbonates of calcium and magnesium, forty-six lysimeters were installed July, 1914. This equipment has been described and illustrated in previous reports (6; 7) upon certain phases of the general problem. The annual and 8-year losses of calcium and magnesium, both direct and as a result of *subsoil interchange* induced by leachings from excessive additions, are given in this contribution. It will be shown also that excesses of solid-phase calcic and magnesian materials in the surface soil are *reversibly repressive* upon the solubility of native stores of the alkali-earths. Certain calcic and magnesian treatments depressed calcium and magnesium outgo decidedly below corresponding losses from the untreated control. A supplementary article will report leaching data from much smaller amounts of calcic and magnesian materials.

EXPERIMENTAL

Each material, CaO, MgO, CaCO_3 , MgCO_3 , limestone, dolomite, and magnesite was used in chemical equivalence at the rates of 8, 32, and 100 tons of CaO per 2,000,000 pounds of moisture-free soil. Each addition was made to surface soil only and to soil underlaid by a 1-foot depth of clay subsoil. One wollastonite and one serpentine addition were also made in deep tanks. All additions were mixed throughout the full depth of the surface soil. The compositions of the additions have been given in a previous (8, p. 2) contribution. The soil used was an acid loam secured from a near-by source. It was protected from drying out during the process of screening, sifting, and admixture of treatment. The surface soil contained 0.18 per cent CaO and 0.30 per cent MgO, while the subsoil contained 0.19 per cent CaO and 0.47 per cent MgO.

Periodic collections of leachings were aliquoted and acidified with HCl to obtain annual composites. One-liter portions of composites were concentrated for the determination of calcium and magnesium by standard methods.

PRESENTATION OF DATA

Each annual and total outgo of calcium from the surface soil alone is shown in juxtaposition to the outgo from surface soil after its passage through subsoil for the additions at the 8-, 32- and 100-ton rates in tables 1, 2, and 3, respectively. Annual and total losses, or retentions, of magnesium are shown in the same manner in tables 4, 5, and 6. Only the totals are considered in this contribution, though nitrates, sulfates, carbonates, bicarbonates and hydroxides have been determined. Since all treatments were based on chemical equivalence, *the losses and increases are expressed throughout as CaCO_3 -equivalence, for both calcium and magnesium.* The totals and the annual averages for the first and second 4-year periods and for the full 8-year period also are given. In the third from the last column of each of the six tables are given the differences between the total losses from the shallow tanks and those from the corresponding deep tanks. Such differences show the direct losses from the excess of the applied calcic or magnesic material, the amount of applied base stopped by the subsoil, and the increase due to liberation of calcium by the base applied in excess to the surface soil.

OUTGO OF CALCIUM FROM TREATMENTS IN FORTY-SIX TANKS

From burnt lime. The maximum loss from the 8- and 32-ton treatments in the shallow tanks came during the first year. The 100-ton addition gave unusually heavy yields during the first three years, with the maximum for the third year. The loss from the light treatments was due entirely to bicarbonate, nitrate, and sulfate of calcium; but considerable $\text{Ca}(\text{OH})_2$ came from the two heavier treatments. More than one-half of the loss from each addition came during the first 4-year period. The total losses during both 4-year periods and during the full period increase in the order of increase of treatment, but not in direct proportion.

The yields from the deep tanks were uniformly less and but a fraction of the yields from corresponding shallow tanks. Differing from the shallow tanks, no $\text{Ca}(\text{OH})_2$ has ever passed through the subsoil. Of the totals, 7194, 9530, and 27,349 pounds from the three rates in the shallow tanks, the subsoil caused respective stoppages of 4270, 7174, and 24,566 pounds.

From burnt magnesia. The MgO treatment proved decidedly depressive to the outgo of calcium from the surface soil. The average annual loss from the shallow control was 205 pounds, while the annual losses from the 8-, 32-, and 100-ton MgO additions were 117, 70, and 68 pounds, respectively. By reference to tables 4, 5, and 6 it will be seen that, coincident with depressed calcium outgo, large quantities of soluble salts of magnesium came from the MgO additions, the outgo increasing with rate of addition. It is an established fact that solutions of neutral salts of the alkalies and alkali-earth metals will effect a liberation of one or more of the soil bases not present in the treatment solution. But the depressive influence of the added MgO upon the surface-

TREATMENT	SUBSOIL	TANK NUMBER	CaCO ₃ EQUIVALENT IN POUNDS PER 2,000,000 POUNDS OF SOIL													
			Annual Periods						8-year period						Decrease in yielded subsoil or yields stopped shallow and deep control tanks	
			First 4-year period		Second 4-year period		Total		First 4-year period		Second 4-year period		Total			
			Average annual yield per year	Total	Average annual yield per year	Total	Average annual yield per year	Total	Average annual yield per year	Total	Average annual yield per year	Total	Average annual yield per year			
1 CaO	None	1767	1062	1009	446	1071	4284	732	764	630	784	728	2910	899	7194	694
22	Clay	499	408	410	197	379	1514	305	391	328	386	353	1410	366	2924	265
2 MgO	None	180	74	164	61	120	479	123	107	105	121	114	456	117	935	88
23	Clay	439	477	442	195	388	1553	306	422	287	374	347	1389	368	2942	267
3 CaCO ₃	None	1406	831	913	453	901	3603	749	750	668	823	748	2990	824	6593	619
24	Clay	350	350	435	174	327	1309	383	483	284	375	381	1525	354	2834	253
4 MgCO ₃	None	189	79	145	56	117	469	113	75	113	128	107	429	112	898	93
25	Clay	388	470	551	180	397	1589	293	432	278	308	328	1311	363	2002	262
5 Limestone	None	1730	818	929	394	968	3871	727	757	724	810	755	3018	861	6889	656
26	Clay	279	407	423	187	324	1296	320	387	285	352	336	1344	330	2640	229
6 Dolomite	None	756	442	395	216	452	1809	455	432	403	490	445	1780	449	3589	244
27	Clay	233	382	366	135	279	1116	260	334	264	292	288	1150	283	2266	172
7 Magnesite	None	402	155	131	58	187	746	112	83	117	166	120	478	153	1224	52
28	Clay	350	436	365	133	321	1284	225	226	236	267	239	954	280	2238	179
46 None	None	280	112	214	299	224	905	122	204	1451	65	163*	326*	1231†	1014	
45	Clay	142	41	87	181	113	53	87	87	87	87	76*	205†	152*	628†	
Rainfall in inches		47.78	56.54	63.32	47.79	53.86		51.41	54.21	50.37	55.63	52.91		53.38		

2-year average
6-year period on

Amounts of calcium salts leached from a loam soil during an 8-year period—Nine calcic and magnesian additions at rates equivalent to 32 tons of lime per 2,000,000 lbs. of soil.

TREATMENT	TAXE NUMBER	SUBSOIL	Annual periods		8-year period		Average annual variation from shallow and deep control tanks		Decrease increase										
			First 4-year period		Second 4-year period		Total												
			Average annual	Total	Average annual	Total	Average annual	Total											
8 CaO	29	Clay	None	2601	1255	478	1422	5689	753	1129	971	988	960	3841	1191	9330	Stopped 7174	986 194	
9 MgO	30	Clay	None	147	21	33	29	58	230	81	15	98	85	70	279	64	509 295	2356 7174	141 194
10 CaCO ₃	31	Clay	None	1309	820	1021	417	892	3567	730	849	718	796	773	3093	833	6660 2953	2236 2444	628 154
11 MgCO ₃	32	Clay	None	130	50	89	41	78	310	85	69	100	90	86	344	82	654 3379	2236 2925	123 347
12 Limestone	33	Clay	None	1330	825	951	445	888	3551	788	752	708	842	773	3090	830	6641 3379	2236 2925	625 347
13 Dolomite	34	Clay	None	1059	686	738	303	697	2786	585	724	510	643	616	2462	656	5248 330	2236 1423	451 229
14 Magnesite	35	Clay	None	270	131	200	85	172	686	142	158	146	152	150	598	161	1284 385	2236 1538	44 274
43 Wollas*	44	Serp.*	Clay	142	367	342	159	253	1010	229	378	267	389	316	1263	284	2273 195	1421† 1560	183 94
<i>Rainfall in inches.....</i>				47.78	56.54	63.32	47.79	53.86	2150	3755	63	52.91	51.41	54.21	53.86	53.33			

* Actual rate of 32 tons of material.

† Yield in excess of 8-year loss from deep control tank 45, 8-year basis.

TABLE 3
Amounts of calcium salts leached from a loam soil during an 8-year period—Seven calcic and magnesian additions at rates equivalent to 100 tons of CaO per 2,000,000 lbs. of soil

				Annual periods				8-year period				Average annual variation from shallow and deep control tanks						
TREATMENT	TANK NUMBER			First 4-year period		Second 4-year period		Total		Subsoil yielded stopped		Decrease						
		First year	Second year	Average annual	Total	Average annual	Total	Average annual	Total	Average annual	Total							
CaO	15	None	5176	5725	8101	1641	5161	20643	2751	1454	1365	1136	1677	6706	3419	27349	Stopped 24566	3214
	36	Clay	159	506	460	201	332	1326	548	345	286	278	364	1457	696	2783	247	247
MgO	16	None	241	57	42	7	87	347	61	61	76	72	68	270	77	617	Yielded 3036	128
	37	Clay	206	679	707	133	431	1725	402	779	387	360	482	1928	457	3653	3036	356
CaCO ₃	17	None	1278	999	913	385	894	3575	658	685	706	675	681	2724	788	6299	Stopped 2640	583
	38	Clay	172	386	346	237	285	1141	369	451	329	350	375	1499	330	3659	3639	229
MgCO ₃	18	None	125	365	44	26	140	560	74	88	89	93	86	344	113	904	Yielded 2462	92
	39	Clay	236	899	1088	126	587	2349	300	306	191	220	254	1017	421	3366	2462	320
Limestone	19	None	1603	859	990	391	961	3843	724	782	694	696	724	2896	842	6739	Stopped 4246	637
	40	Clay	347	418	267	143	294	1175	271	425	313	309	330	1318	312	2493	4246	211
Dolomite	20	None	1262	741	832	332	792	3167	701	760	648	713	706	2822	749	5989	Stopped 2992	544
	41	Clay	233	291	269	133	232	926	466	594	440	566	517	2066	374	2997	2992	273
Magnesite	21	None	419	172	217	79	222	887	147	165	160	176	162	648	192	1535	Yielded 2708	13
	42	Clay	196	419	432	182	307	1229	345	464	342	328	370	1479	376	1173	2708	275
Rainfall in inches.....		47.78		56.54		63.32		47.79		53.86		51.41		54.21		55.63		53.38

Amounts of magnesium salts leached from a loam soil during an 8-year period—Seven calcic and magnesian additions at rates equivalent to 8 tons of CaO per 2,000,000 lbs. of soil

TREATMENT	TANK NUMBER	SEASON	CaCO ₃ EQUIVALENT IN POUNDS PER 2,000,000 POUNDS OF SOIL.														
			Annual periods						8-year period						Increase	Decrease	
			First 4-year period			Second 4-year period			Average annual			Total					
			First year	Average	Total	Fourth year	Fifth year	Sixth year	Seventh year	Eighth year	Average annual	Total	Subsoil or yield stopped	Yielded			
1 Cao	1	None	112	61	36	39	62	248	44	84	59	61	242	61	490	45	
22 Clay	22	Clay	279	300	323	165	267	1067	260	444	267	310	1241	269	2308	132	
2 MgO	2	None	2274	1346	1448	570	1410	5638	817	998	613	723	788	3151	1099	8789	993
23 Clay	23	Clay	239	361	374	252	307	1226	240	418	276	334	317	1268	312	2494	175
3 CaCO ₃	3	None	149	58	74	48	82	329	48	172	59	36	79	315	81	644	25
24 Clay	24	Clay	184	250	356	205	249	995	301	487	307	304	350	1399	299	2394	162
4 MgCO ₃	4	None	3525	1791	1569	631	1879	7516	787	977	712	759	809	3235	1344	10751	1228
25 Clay	25	Clay	210	338	480	231	315	1259	298	504	330	368	375	1500	345	2759	208
5 Limestone	5	None	163	71	71	37	86	342	53	149	43	107	88	352	87	694	19
26 Clay	26	Clay	171	293	369	142	244	975	240	403	270	262	294	1175	269	2150	132
6 Dolomite	6	None	484	384	345	195	352	1408	351	468	320	463	401	1602	376	3010	270
27 Clay	27	Clay	161	276	350	146	233	933	229	352	239	246	267	1066	250	1999	113
7 Magnesite	7	None	1595	1064	1139	533	1083	4331	789	1043	716	791	835	3339	959	7670	853
28 Clay	28	Clay	205	343	358	170	269	1076	212	272	216	255	239	955	254	2031	117
46 None	46	None	126	94	70	136	107	426	80	128	78	89	104	208*	106†	634†	
45 Clay	45	Clay	226	86	133	208	163	653	78	89	84	84	137†	820†	186†	Yielded	
Rainfall in inches.....			47.78	56.54	63.32	47.79	53.86								53.38		
															52.91		

* Two years.
† Six years.

TABLE 5
TABLES OF MAGNESIUM SALTS LEACHED FROM A LOAM SOIL DURING AN 8-YEAR PERIOD—NINE CALCIC AND MAGNESIC ADDITIONS AT RATES EQUIVALENT TO 32 TONS CaO PER 200,000 LBS. OF SOIL

TREATMENT	TANIE NUMBER	SUBSOIL	Annual periods						8-year period			Annual average variation from shallow and deep control tanks				
			First 4-year period		Second 4-year period		Total		Average annual		Subsoil or yielded stopped					
			Average annual	Total	Average annual	Total	Average annual	Total	Average annual	Total	Decrease					
CaO	8 29	None Clay	73 88	51 432	26 508	43 167	193 299	88 1195	130 220	48 299	331 896	66 261	40			
MgO	9 30	None Clay	3749 119	5024 884	4869 2105	1735 762	3847 968	15387 3870	1595 866	2037 1575	1455 1339	1372 933	1615 1178	124		
CaCO ₃	10 31	None Clay	114 152	84 272	91 304	55 139	86 217	344 867	33 215	166 404	90 302	89 279	88 300	18		
MgCO ₃	11 32	None Clay	3878 390	3944 865	4969 2306	2678 1806	3867 1342	15469 5367	3403 1689	4081 3290	3246 2241	3410 2068	3535 2323	2625		
Limestone	12 33	None Clay	148 157	82 276	93 287	64 139	97 215	87 859	84 236	1523 408	100 272	125 216	99 283	936		
Dolomite	13 34	None Clay	525 211	383 288	442 390	173 167	380 264	1056 262	298 295	490 293	276 294	368 311	358 1244	121		
Magnesite	14 35	None Clay	1138 237	1095 313	1361 489	671 288	1066 332	4265 1327	888 311	1212 441	836 301	945 328	970 345	1018 1381	138	
Wollas.*	43	Clay	176	298	352	150	244	976	229	396	273	326	306	275 202	1496 808	109†
Serp.*	44	Clay	94	194	250	150	172	688	112	292	173	231	202	187 187	1496 808	50
<i>Rainfall in inches.....</i>			47.78	56.54	63.32	47.79	53.86			51.41	54.21	50.37	55.63	52.91	53.38	

TABLE 6
Amounts of magnesium salts leached from a loam soil during an 8-year period—Nine calcic and magnesian additions at rates equivalent to 100 tons CaO per 2,000,000 lbs. of soil

TREATMENT	TANK NUMBER	soil	Annual periods												Annual average variation from shallow and deep control tanks			
			First 4-year period				Second 4-year period				8-year period				Subsoil yielded or yielded stopped	Increase	Decrease	
			Average annual	Total	Average annual	Total	Average annual	Total	Average annual	Total	Average annual	Total	Average annual	Total				
15	CaO	None	71	37	51	20	45	179	42	133	35	44	64	254	54	433	Yielded	52
36		Clay	140	380	402	503	356	1425	324	324	310	145	276	1103	316	2528	{ 2095	179
16	MgO	None	2002	3456	3377	1216	2513	10051	3046	5494	3999	3246	3946	15785	3220	25336	{ Stopped	3114
37		Clay	181	520	648	562	478	1911	929	4035	3639	2848	2863	11451	1670	13362	{ 12474	1533
17	CaCO ₃	None	258	240	163	58	180	719	89	225	101	124	135	539	157	1258	{ Yielded	51
38		Clay	120	279	299	208	227	906	284	462	307	283	334	1336	280	2242	{ 984	143
18	MgCO ₃	None	4537	5048	6018	2238	4460	17841	3719	5149	3886	3897	4163	16651	4312	34492	{ Stopped	4206
39		Clay	179	700	2938	1896	1428	5713	2739	4450	3605	3220	3504	14014	2466	19727	{ 14765	2329
19	Limestone	None	214	105	168	56	136	543	90	127	109	95	105	421	121	964	{ Yielded	15
40		Clay	257	349	294	132	258	1032	245	423	290	292	313	1250	285	2282	{ 1318	148
20	Dolomite	None	525	382	407	163	369	1477	307	443	304	336	348	1390	358	2867	{ Stopped	252
41		Clay	137	251	287	134	202	809	378	522	340	146	347	1386	274	2195	{ 672	137
21	Magnesite	None	1323	1084	1316	564	1072	4287	784	1111	812	896	901	3603	986	7890	{ Stopped	880
42		Clay	100	333	413	212	265	1058	307	487	357	350	375	1501	319	2539	{ 5340	182
		Rainfall in inches.....	47.78	56.54	63.32	47.79	53.86		51.41	54.21	50.37	55.63	52.91			53.38		

soil outgo under field conditions, intimate admixture of the solid phase and diffusion of the bicarbonate and neutral salts of magnesium, is different from the results to be anticipated when excess of dissolved salts are agitated with surface soil and is not in harmony with the accepted concept relative to liberation of calcium by an excess of magnesium. It is in harmony, however, with previous lysimeter findings (7, 10), in which it was shown that magnesic, and also calcic materials proved depressive, rather than liberative, to the outgo of potassium salts.

The reverse condition obtained when the magnesium leachings from the surface soil passed through the subsoil. Without exception, all twenty-four annual-leaching composites from the MgO additions in the deep tanks carried decidedly larger amounts of calcium than those leached from the corresponding shallow tanks. Furthermore, *the CaCO₃ liberated by the 8-ton MgO treatment was greater than the CaCO₃ recovery from the 8-ton CaO addition and still greater than that from the addition of CaCO₃ at the same rate. The two heavier MgO additions both liberated still more of CaCO₃ from the subsoil than was obtained as recoveries as soil-subsoil leachings from either the 32- or 100-ton additions of CaO and CaCO₃.* For the total period, the accumulations of CaCO₃ during the movement of leachings through the subsoil were 2007, 2444, and 3036 pounds, respectively, for the 8-, 32-, and 100-ton MgO additions. These results give corresponding annual averages of 251, 306, and 380 pounds CaCO₃-equivalence, as representing the cumulative effect of the subsoil with influx of magnesium salts, as against the 101-pound average annual loss, or about one-half of the 205-pound increment leached to it from the untreated surface soil. Applying the actual blank of the deep tank, the average annual yields of CaCO₃ from the subsoil appear as 267, 268, and 356 pounds, for the three additions, in order.

The difference between the shallow- and deep-tank calcium losses from MgO treatments are so striking and consistent as to warrant some attempt at explanation. Several possibilities suggest themselves. In view of the insolubility of Mg(OH)₂, it may be assumed that the depression exerted by solution phases are to be attributed rather to the bicarbonate, nitrate, or sulfate of magnesium. If the calcium content of the subsoil were greater than that of the surface soil there would be expected a greater CaCO₃ liberation. But the respective contents of 0.18 per cent and 0.19 per cent eliminate this consideration as a causative factor. Again it may be that the solubility of the calcium compounds in the subsoil is greater than that of those in the surface soil, the subsoil being uniformly in a more hydrolytic condition. On the other hand, the conditions under which the added material is brought into contact with the soil mass through solution varies for the upper and lower soil. The surface zone of the soil often may be so dry as to preclude free movement of solvent and solute, and when free movement does obtain after rainfall, it is more rapid and the period of contact is therefore of less duration than in the case of the subsoil. Furthermore, the volume of the subsoil

stratum is greater, the subsoil depth being 12 inches as against approximately 8 for the surface soil. It may be, therefore, that the difference between non-replacement in the surface soil and interchange in the subsoil is due largely to difference in bulk and to the time factor. The lysimeter results demonstrate the facts as found under the experimental conditions, with emphasis upon excessive treatment, but supplementary laboratory investigations are necessary and are now in progress, to clarify the problem.

From calcium carbonate. The three rates show close concordance where the precipitated material was used as a control against the burnt lime in the shallow tanks. The period averages and the totals show but little variation as a result of the range of the treatment from 8 to 100 tons. The three totals of 6593, 6660, and 6290 pounds indicate that the 8-ton addition was so uniformly disseminated throughout the mass of the soil as to insure maximum solvent action under the prevailing conditions. Assuming an H_2CO_3 constant, the somewhat smaller outgo from the 100-ton treatment may be assigned to physical causes incident to the increase in bulk resultant from the heavy addition. Each of the three additions gave surface-soil losses less than those obtained from the respective CaO equivalents. The greater disparities, which followed increase in rate were due more to the leachings of $Ca(OH)_2$ from the CaO than to any lack of equivalence in outgo of calcium bicarbonate. Each annual outgo through the subsoil was distinctly less than the amount obtained from the surface soil alone. The subsoil stopped $CaCO_3$ at the rates of 2759, 4424, and 3659 pounds, respectively, for the 8-, 32-, and 100-ton additions. As pointed out in a previous contribution (8), this agreement between yields from the 8- and 100-ton treatments, the slower movement, smaller outgo, and greater retention by the subsoil were consistent, the same relationships obtaining, so far as determined, for nitrate and sulfate of calcium, as well as bicarbonate.

From magnesium carbonate. Magnesium carbonate exerted the same positive depressive influence as that exerted by MgO upon the outgo of calcium from the surface soil, though on the whole not to the same degree. In no case did the total $CaCO_3$ yield from the $MgCO_3$ -treated soil approach that from the untreated surface soil. Again, as in the MgO tanks, the $MgCO_3$ treatment effected a distinct liberation of $CaCO_3$ from the subsoil, so that the $CaCO_3$ passing from the $MgCO_3$ tank was actually greater than that from the tank which received $CaCO_3$ at the 8-ton rate. This was also true, to an even greater extent, in the case of the 32- and 100-ton additions. On the previously mentioned assumption that applied MgO is inactive as the hydroxide because of the meager amounts of $Mg(OH)_2$ carried in the free soil water, and that the depression in calcium outgo is caused by bicarbonate, nitrate, and sulfate of magnesium, the discussion devoted to the outgo of calcium salts from MgO additions is applicable also to leachings from the $MgCO_3$ additions.

From 100-mesh limestone. The 100-mesh limestone, containing 94.33 per cent $CaCO_3$ and 1.62 per cent $MgCO_3$, gave a $CaCO_3$ yield intermediate be-

tween that from CaO and that from the precipitated carbonate at the 8-ton rate in the shallow tanks. The total recoveries of 6889, 6641, and 6739 pounds from the 8-, 32-, and 100-ton treatments show that no increase in outgo resulted from increase in rate of application. In like manner the several amounts arrested by the subsoil demonstrate the uniformity of its tendency to absorb when it receives comparable amounts from the surface-soil leachings. From the surface-soil yields of 6889, 6641, and 6739 pounds of CaCO₃ for the treatments, in order, 4249, 4288, and 4246 pounds were stopped.

From 100-mesh dolomite. The dolomite contained 49.96 per cent CaCO₃, 39.11 per cent MgCO₃. The amounts of CaCO₃ leached from it were therefore uniformly less as annuals and totals for the shallow tanks. Differing from the leachings from limestone additions, the dolomite additions gave increased outgo of calcium with increase in treatment. Although the amounts from the shallow tanks were uniformly more than those from the corresponding deep tanks, for all three rates, the differences were not so large as those which were found in the limestone series. With increase in rate, there was an increase also in the amount of CaCO₃ removed from solution by the subsoil, the 8-, 32-, and 100-ton additions having shown removals of 1323, 2612, and 2992 pounds, respectively.

From 100-mesh magnesite. The less soluble magnesite did not show so extensive a retardation in CaCO₃ outgo from the surface soil as that shown by MgO and by MgCO₃ at the three rates. Nevertheless, the totals and annual averages showed positive depressive influences. Such were in effect more particularly after the first two years. The deep tanks showed CaCO₃ losses consistently greater than those found for the corresponding shallow tanks and also controls. The average total of CaCO₃ increase from the subsoil was comparable to the outgo from the soil, practically one-half of the amount leached from the 8-ton additions of MgO and MgCO₃, and 35.8 per cent of that derived by the solution and leaching of the corresponding CaCO₃ addition to the surface soil. Differing from the MgO, which gave increased liberation with increase in rate, and agreeing with the MgCO₃, the largest outgo of CaCO₃ from the subsoil came from the 32-ton treatment, which yielded 1713 pounds, as against 1014 pounds and 1173 pounds for the 8- and 100-ton additions respectively.

From 100-mesh wollastonite and serpentine. These two materials were used only in the deep tanks. The wollastonite contained 45.11 per cent CaO, 0.48 per cent MgO, and 0.69 per cent CO₂, while the serpentine contained 0.09 per cent CaO, 37.79 per cent MgO, and 0.14 per cent CO₂. After the first year all composites of leachings from the wollastonite carried more calcium salts than did the corresponding composites from serpentine. However both materials gave a larger annual average outgo of CaCO₃ than that from the deep control tank—284 pounds, 195 pounds, and 101 pounds for wollastonite, serpentine, and control, respectively. It is thus apparent that some of the wollastonite-derived calcium salts passed through the subsoil and

that the serpentine-derived magnesium compounds liberated each year about 100 pounds of CaCO_3 from soil, or subsoil, or both. Since magnesite exerted the same depressive tendency manifested by the more rapidly dissolved MgO and MgCO_3 upon the outgo of calcium salts from the surface soil, it is more probable that the increase in CaCO_3 above the yield from the control was due to an interchange induced in the subsoil by the serpentine-derived magnesium salts. When calculated to an 8-year loss, the outgo of 802 pounds of CaCO_3 -equivalence falls 1471 pounds short of that from the wollastonite. In the same manner, an increase of 758 pounds is attributed to the magnesium silicate of the serpentine. For each CaCO_3 -pound-equivalent leached from the surface and through the subsoil, there was an interchange yield of 0.515 pound induced by the serpentine.

OUTGO OF MAGNESIUM FROM FORTY-SIX TANKS

It is readily conceded that a solution of neutral salts will effect an interchange of magnesium in the components native to the soil. Very few data are available, however, as to the activity of CaO and CaCO_3 under conditions comparable to those of the field.

MacIntire (5) analyzed the three upper 7-inch zones of the limed plots of the Pennsylvania Experiment Station, after thirty-years of cumulative liming. The samples analyzed were composites of the plots of tiers 1-4, which received burnt lime, burnt lime plus manure, and ground limestone. It is of course admitted that the results so obtained were subject to the error incident to the sampling of so large a total area—one-half acre—for each treatment and to the variation in soil type. The ultimate analyses showed, however, that both lime and limestone had caused a uniform decrease in residual magnesium. The magnesium content of the check plots, and also that of the composites from both forms of lime, increased with depth. This indicated that the treatment had been of effect in the surface soil and of minimum effect upon the subsoil; or that it had been of effect in the surface soil with the subsoil showing stoppage of part of the induced loss from the surface. Lyon and Bizzel (3) found that applications of lime increased the magnesium content in the leachings from a Dunkirk clay loam in 4-foot tanks. Their results are consistent as indicating basic exchange in some zone, or all zones, of the 4-foot depth, the magnesium content of which increases with increase in depth. They do not determine, however, whether the magnesium was derived from the surface or subsoil. The same investigators found similar evidence of basic exchange in studies with 4-foot depths of Volusia silt loam, which differed from the Dunkirk soil in that the three subsoil strata contained less magnesia than did the surface soil.

From burnt lime. The outgo of magnesium salts from the three CaO additions in the shallow tanks was uniformly less than that of the shallow control. The 8-year totals of 490, 524, and 433 pounds for the 8-, 32-, and 100-ton additions represent average annual leachings of 61, 66, and 54 pounds, respectively, as against 106 pounds from the control. The three lime treatments therefore caused annual conservations of 45, 40, and 52 pounds, respectively. The consistent depressive influence was changed, however, to an accelerative activity when the dissolved calcium salts reached the subsoil. Each of the twenty-four annual leachings from the soil-subsoil tanks carried

a magnesium content greater than that from the corresponding surface tank and a decided excess over the outgo from the control. The amounts of magnesium salts forced from the subsoil, as shown by the differences between surface soil and soil-subsoil leachings, were 1818, 1567, and 2095 pounds, respectively, or annual averages of 132, 124, and 179 pounds in *excess* of the control for the 8-, 32-, and 100-ton additions.

The unabsorbed portion of the 8-ton CaO treatment remained in the hydrate form only a short time, but hydrate excesses were present for over three years where the heavier additions of 32 tons and 100 tons were made, as was shown by periodic residual carbonate determinations and by the determination of $\text{Ca}(\text{OH})_2$ in leachings. But such occurrences failed to show any liberation of magnesium from the surface soil. It could not be assumed that there occurred a liberation of magnesium as the hydrate and that in this insoluble form the magnesium was retained by the soil. For since the MgO parallel demonstrated that large quantities of MgO were carbonated and leached, much if not all of such assumed $\text{Mg}(\text{OH})_2$ would have leached as the bicarbonate after the conversion of the insoluble magnesium hydrate into hydroxide and then into the soluble bicarbonate, thereby showing a larger magnesium outgo during the second 4-year period. However, the losses during the second 4-year period were relatively the same as those of the first 4-year period. Furthermore, the calcium carbonate influenced magnesium outgo in the same manner. Again, if the repressive action were to be considered as due to mechanical protection afforded the native magnesian components by the added calcic forms, the much heavier additions of oxide and carbonate at the 32- and 100-ton rates would be expected to be still more retardative than the 8-ton rate; but such proved not to be the case. Although plausible viewpoints might be advanced to explain the failure of the soluble hydrate and the lesser soluble carbonate of calcium to liberate magnesium from the soil, it is difficult to account for the fact that instead of liberation, or non-liberation, there was a positive and consistent removal of magnesium from the solution phase in the soil mass.

From burnt magnesia. The most rapid outgo of magnesium salts from the 8-ton treatment came during the first three years, with the maximum during the first year. A large part of the loss from the surface soil was stopped by the layer of subsoil during each of the eight years. From a comparison of the totals of 8789 pounds and 2494 pounds from the shallow and deep tanks, respectively, it appears that the subsoil retained 6295 pounds of soluble magnesium salts. Similar differences from the 32-ton and 100-ton additions show the subsoil to have absorbed 13,263 pounds from the former and 12,474 pounds from the latter. The MgO-CO₂-H₂CO₃ balances of the two heavier treatments differed from that of the 8-ton addition and between themselves, in the shallow-tank leachings. The greatest yearly losses from the 32-ton treatments came during the first three years, as was true of the 8-ton yield; but both the second and third years' losses were in excess of the loss of the

initial year. During the next five years the losses varied from a minimum of 1372 pounds during the eighth year to a maximum of 2037 pounds during the sixth year. But the 2002-pound outgo from the 100-ton treatment during the initial year was the smallest of the losses of the first three years and but two-thirds of the minimum of the annual losses of the second 4-year period. The total outgo from the 32-ton shallow tank was $1\frac{1}{2}$ times greater than that from the shallow 100-ton tank for the first 4-year period, but for the second 4-year period only about 40 per cent of that from the 100-ton treatment. These differences are most probably due to the fact that the excess of oxide in the larger treatment accounted for the CO_2 available by the formation of more MgCO_3 and less $\text{MgH}_2(\text{CO}_3)_2$ than in the 32-ton treatment.

The soil-subsoil leachings from the 8-ton addition showed more uniformity in magnesium content throughout the 8-year period than did either of the two heavier additions. After the minimum of the initial year the movement from the 32-ton addition increased decidedly, with maintenance of a larger-proportion relationship to the outgo from the surface soil. Following the minimum of the initial year, the 100-ton addition gave about threefold increases during the succeeding 3 years. The losses for the second, third, and fourth years, however, were less than the corresponding losses from the 32-ton addition. A distinct increase in magnesium leachings from the 100-ton deep tanks occurred during the fifth year, but the still larger increases during the last three years of the 8-year period were such as to cause the subsoil leachings of magnesium to approach those from the surface soil. With this tendency maintained, the 100-ton losses will soon equal and surpass those from the 32-ton additions. It was interesting to observe during the progress of the investigation that the presence of distinct increases in both neutral salts and bicarbonate of magnesium appeared in the subsoil leachings of the 32-ton addition before such were noted in the leachings from either the 8-ton or 100-ton additions.

From calcium carbonate. After the first year, the CaCO_3 treatments at the 8- and 32-ton rates showed the same tendency as that exerted by CaO in depressing the outgo of magnesium from the shallow tanks. The average annual losses from these two rates were 81 pounds and 88 pounds, as against 106 pounds from the shallow control, corresponding to annual depressions of 25 pounds and 18 pounds. The average annual loss of 157 pounds of CaCO_3 from the 100-ton shallow tank shows that an annual liberation of 51 pounds was effected by the 100-ton treatment. The average annual losses for the first and second 4-year periods were in close agreement, 82 pounds and 81 pounds for the 8-ton addition and 86 pounds and 88 pounds for the 32-ton addition.

The outgo of magnesium through each deep tank was larger than that from the corresponding shallow tank during each of the eight annual periods for both 8- and 32-ton additions and for the last seven of the eight annual periods in the case of the 100-ton treatments. The amounts of magnesium forced

out from the subsoil by the influx of surface-soil calcium salts came in the order of 8, 100, and 32 tons. Because of the larger amount of magnesium leached from 100-ton treatment in the surface soil, however, the amounts of magnesium derived from the subsoil come in the order of 8, 32, and 100 tons. The average annual supplements to the leachings from the surface soil, as supplied by the subsoil, were 31 pounds for the subsoil control and 218 pounds, 170 pounds, and 123 pounds where the influences of the 8-, 32-, and 100-ton additions were, respectively, of effect. The actual annual increases above the outgo from the control were 162 pounds, 121 pounds, and 143 pounds for the additions, in order.

From magnesium carbonate. By far the largest annual outgo of magnesium from the 8-ton addition of this treatment in the shallow tank was obtained during the first year. Approximately 70 per cent of the total outgo for the 8 years was obtained during the first 4-year period. The major portion of the outgo came as a result of the hydrolysis of magnesium silicates, the full addition of the carbonate soon having been converted to those forms. Five of the eight annual yields from the 32-ton addition to the shallow tank were in excess of the initial and maximum annual outgo from the 8-ton addition; while the remaining three annual losses were far in excess of the next to the largest annual outgo from the 8-ton addition. The excess of magnesium carbonate at this rate was such as to afford large quantities of the hydrated carbonate for solution in the free soil water. Of the grand total outgo, 52.2 per cent was obtained during the first four years. With the exception of the fourth year, each annual outgo from the 100-ton addition was in excess of the corresponding annual yield from the 32-ton addition. Of the 8-year surface-soil loss of 34,492 pounds for the 8-year period, 17,841 pounds, or 51.7 per cent, passed out during the first 4-year period. The actual annual outgo induced by treatment, as determined by subtraction of the average annual outgo of the surface control, was 1228 pounds for the 8-ton addition, 2595 pounds for the 32-ton addition, and 4206 pounds for the 100-ton addition.

Though the several magnesium salts were readily derived from the non-carbonate forms resultant from the absorption of the 8-ton addition in surface soil, they were in large part absorbed by the subsoil, without evidence of any diminution in this property at the end of the 8-year period. Nevertheless, the absorption by the subsoil was not absolute, for the 345-pound annual average outgo was 208 pounds in excess of the 137-pound loss from the control. Although the stoppage by the subsoil was much greater for the 32-ton and 100-ton additions than for the 8-ton addition, the proportion between losses from soil and soil-subsoil were not so large for the heavier additions. Of the totals of 10,751, 29,609, and 34,492 pounds which passed from the additions of 8, 32, and 100 tons, respectively, in the surface soil, the amounts retained by the subsoil—7992, 14,954, and 14,765 pounds—represented respective per cent equivalents of 74.3, 50.5, and 42.8. The average annual

increases in outgo above the loss from the deep control were 208, 1695, and 2329 pounds for the three treatments, in order. The amounts of treatment leachings absorbed during the first 4-year period were greater, for each rate, than the corresponding amounts retained during the second 4-year period. The subsoil absorbed during the first 4 years 6257, 10,102, and 12,128 pounds from 8, 32, and 100 tons, respectively, as against 1735, 4852, and 2637 pounds, during the second 4-year interval.

From 100-mesh limestone. The general tendency of the 8-ton-limestone addition was to depress the outgo of magnesium from the surface soil, the annual average of 87 pounds being less than that of 106 pounds from the control. In agreement with CaCO_3 , the addition of the maximum amount caused a reversal in this relationship, while the yield from the 32-ton addition was very close to that from the untreated soil.

Applying the average annual outgo from shallow control to the three treatments, in order, depression of 19 pounds per annum was shown for the 8-ton addition and increases of 5 and 15 pounds, respectively, for the two heavier amounts.

After the first year all of the subsoil leachings from limestone at the three rates carried more magnesium than did those from the corresponding surface soil, and also more than those from the soil-subsoil control. With increasing order of treatment the yields of magnesium from the subsoil were 1456, 1105, and 1318 pounds. After deduction of the average annual from the deep tank, these three amounts represent actual subsoil releases of 132, 112, and 148 pounds per annum, respectively.

From 100-mesh dolomite. All annual losses from the surface soil which received the three dolomite treatments were in excess of the corresponding losses from the shallow control. Increase in rate of additions gave no increases in total outgo from the surface soil. The totals of 3010, 2975, and 2867 pounds for the 8-, 32-, and 100 ton treatments, respectively, represent average annual losses of 376, 372, and 358 pounds, as against 106 pounds from the control, or net corresponding losses of 270, 266, and 252 pounds.

The subsoil leachings from the dolomite are distinctive, as differing from those of the other eight oxide, carbonate, and silicate forms. In all of the other eight materials either calcium or magnesium was a preponderant component and this relationship obtained in their carbonated-water solutions. As a result, there was in every case a yield of one base and stoppage of the other, as will be seen by comparisons between the third from the last columns of tables 1 and 4, 2 and 5, and 3 and 6. But the CaCO_3 and MgCO_3 content of the dolomite were on a near-parity. The magnesium carbonate content of 39.11 per cent, equivalent to 46.42 per cent CaCO_3 , gives a ratio of 1:1.08. Carbonated water extractions of this dolomite showed that the two carbonates dissolved in practically the proportion in which they occur in the rock. There was therefore a stoppage of both calcium and magnesium by the subsoil underlying 3 of the 6 dolomite additions. It is interesting to observe that the surface-

soil losses of magnesium from the dolomite additions were not correlated with rates, and that the calcium outgo increased with increase in treatment. Without deduction of the yield from the shallow control, the ratio of magnesium, in chemical equivalence, found in the leachings was 1:1.19 for the 8-ton addition, 1:1.76 for 32 tons, and 1:2.09 for 100 tons. Applying correction for the average annual of magnesium and calcium from the control, the ratios of $MgCO_3$ to $CaCO_3$, based on chemical equivalence, are 1:0.90, 1:1.70, and 1:2.08 for the 8-, 32-, and 100-ton additions, respectively. In the deep-tank leachings, the ratios of $MgCO_3$ to $CaCO_3$, on chemically equivalent basis, were found to be 1:1.13, 1:1.15, and 1:1.36 for 8, 32, and 100 tons, respectively, as a result of the absorptive influence of the subsoil. Applying the average annual outgo of 137 pounds of $MgCO_3$ and that of 101 pounds of $CaCO_3$ from the deep-tank control, the corresponding ratios of $MgCO_3$ to $CaCO_3$, on chemical equivalence basis, are 1:1.61, 1:1.52 and 1:1.99.

From 100-mesh magnesite. Each annual outgo of magnesium from the shallow tanks at the three rates was decidedly increased (about ninefold) where magnesite additions were made. The totals for the first 4 years were very close, 4331, 4265, and 4287 pounds, respectively, for the 8-, 32-, and 100-ton treatments, while the corresponding yields for the full 8-year period were 7670, 8146, and 7890 pounds. These results show the surface-soil outgo to be independent of increase in rates within these limits. Corrected for the average loss of 106 pounds from the control, the three magnesite additions yielded yearly averages of 853, 912, and 880 pounds.

Each of the twenty-four annual subsoil leachings contain a much larger amount of magnesium salts than the corresponding leaching from the surface soil. A part of each total surface outgo, however, passed through the subsoil. The three treatments showed average annual losses of 254, 339, and 319 pounds, in order, as against 137 pounds from the deep control, or actual treatment yields of 117, 202, and 182 pounds. The differences between the totals for each pair of shallow and deep tanks showed absorptions of 5539, 5438, and 5331 pounds, respectively. When compared with the stoppage exerted upon the leachings from MgO and $MgCO_3$, the results show that within so wide a range of concentrations of magnesium salts, there is both movement through and absorption by the subsoil. The extensive absorptions of 14,765 pounds from $MgCO_3$ at the 32-ton and 100-ton rates were nearly three times as great as the maximum of 5539 from the three magnesite treatments. Nevertheless, with this demonstrated absorption coefficient, considerable fractions of the magnesite-derived magnesium salts leached through the subsoil.

From 100-mesh wollastonite and serpentine. The calcium salts derived from the wallastonite in the surface zone displaced more magnesium from the subsoil than was contained in the leachings from the deep control tank. The magnesium outgo induced by the wollastonite was actually 1½ times that which resulted from the magnesium silicate of the serpentine addition. The

increase in outgo of magnesium salts per annum from the serpentine addition was 50 pounds, which shows that with less concentrations of magnesium salts in the leachings, the subsoil permitted their downward movement, though the clay may be far from saturated. Based on the 8-year calculation from the 6-year outgo from the deep control, the calcium silicate of wollastonite caused an increased outgo of 1109 pounds CaCO₃-equivalent of magnesium salts through the subsoil, while the corresponding increase from the magnesium silicate of the serpentine treatment was only 405 pounds. Thus for each CaCO₃-equivalent pound of magnesium salts resulting from displacement by the calcium salts derived from the added calcium silicate, there was a direct yield of 0.365 pound from the added magnesium silicate. The lesser solubility of this particular serpentine, as compared with the readily hydrolyzed wollastonite, was established by carbonated water extractions. In this instance, however, the lesser solubility may be accentuated by a larger proportional absorption of the leachings from the serpentine, buffered by only about one-half as much of calcium salts as were present in the wollastonite leachings.

TOTAL CALCIUM-MAGNESIUM OUTGO FROM LIMESTONE AND DOLOMITE

The six limestone tanks and the six tanks containing dolomite afford opportunity for interesting comparisons as to the outgo of total calcium-magnesium salts. The limestone used is more soluble than the dolomite and of course has a much greater calcium-to-magnesium ratio. It will be remembered that the six materials other than dolomite show an enhanced outgo from the surface soil and absorption by the subsoil of the alkali-earth applied in excess. The subsoil absorption of a large part of the excess of outgo from surface treatment was followed by basic exchange in the subsoil. But in the case of the dolomite additions the subsoil effected removal of both calcium and magnesium from the drainage waters. The comparable surface-soil losses of 6889, 6641, and 6739 pounds from the 8-, 32-, and 100-ton treatments, respectively, of limestone resulted in comparable corresponding estopments of 4249, 4288, 4246 pounds when the leachings passed through the subsoil. The calcium outgo from both shallow and deep dolomite tanks, however, increased with increase in additions. The surface losses of 3589, 5248, and 5989 pounds from the three rates, in order, gave corresponding subsoil leachings, which carried 2266, 2636, and 2992 pounds. Since the preparation of this manuscript Morse (11) has made a contribution explanatory of the uniformity of outgo from the reserve fractions of the several limestone additions. The parallel of increase in additions and outgo may be accounted for possibly by the lesser solubility of the dolomite being offset by the greater surface afforded through increase in bulk of treatments.

- * The data of table 7 show the relationship between the total calcium-magnesium leachings from limestone and those from dolomite. The comparative uniformity of both calcium and magnesium outgo from the 3 limestone

additions in the shallow tanks is responsible for totals of 7583, 7527, and 7703 pounds, in order. This shows the outgo to be independent of the reserve stores of carbonate within the two extremes used. The average annual outgo of magnesium from the surface soil containing the three rates is 106 pounds, or exactly that from the shallow control. This demonstrates that no liberation of magnesium was brought about in the surface soil by the treatment. On the other hand, along with increase of calcium from the increase in dolomite additions, the surface soil gave a near-constant yield of magnesium. Because of the near-constant outgo of magnesium and the increase in losses of calcium, the dolomite showed total surface-soil losses of 6599, 8223, and 8856 pounds for the three additions, in ascending order. Thus, in the minimum treatment, the less soluble dolomite gave a surface-soil total outgo

TABLE 7

Total calcium-magnesium outgo from chemically equivalent amounts of 100-mesh limestone and dolomite in a loam soil—losses expressed as lbs. CaCO₃ per 2,000,000 lbs. of soil

	LIMESTONE			DOLOMITE		
	8 tons	32 tons	100 tons	8 tons	32 tons	100 tons
	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
<i>From tanks without subsoil:</i>						
Calcium.....	6889	6641	6739	3589	5248	5989
Magnesium.....	694	886	964	3010	2975	2867
Total.....	7583	7527	7703	6599	8223	8856
<i>From tanks with subsoil:</i>						
Calcium.....	2640	2353	2493	2266	2636	2992
Magnesium.....	2150	1991	2282	1999	2300	2195
Total.....	4790	4344	4775	4265	4936	5187
Stopped by subsoil.....	2793	3183	2928	2334	3287	3669

less than that from the more soluble limestone, but the reverse was true in the case of the 32-ton and 100-ton additions. Again in the case of the amounts of the two bases passing from the limestone treatments and through the subsoil, the losses appeared to be independent of rate of treatment, though replacement of magnesium in the subsoil was indicated in each instance. Hence, the subsoil yields of 2793, 3183, and 2928 pounds of total calcium-magnesium salts showed no relation to rate of treatment. But in the case of dolomite additions, the increases of calcium losses from the subsoil reflected the surface-soil parallel of increase in dolomite treatment and increase in calcium leachings. Therefore, as differing from the limestone outgo of total salts of calcium and magnesium through the subsoil, the dolomite totals from the subsoil increase with increase in additions. The average total leachings through the subsoil from the three additions of limestone and

dolomite were very close, 2141 pounds for the former and 2165 pounds for the latter.

SUMMARY

Calcium and magnesium leachings from 46 lysimeters over an 8-year period are reported. Treatments of CaO, MgO, CaCO₃, limestone, dolomite, and magnesite, in chemical equivalence, at three rates, were made to both deep and shallow tanks. Wollastonite and serpentine were also used in deep tanks. In summarizing, totals only are considered.

Increase in additions of CaO caused increases in outgo of calcium salts from both soil and soil-subsoil, and also increases in the amounts absorbed by the subsoil. Each lime addition caused depression in outgo of native magnesium from the surface soil and liberation of magnesium from the subsoil.

Each MgO treatment depressed the outgo of calcium from the surface soil and liberated from the subsoil more calcium than was leached from the corresponding CaCO₃ additions. The amounts of magnesium leached from the surface and the amounts stopped by the subsoil increased with rates of additions.

The outgo of calcium salts from CaCO₃ in the surface soil was found to be independent of the reserves of unabsorbed carbonate, for both shallow and deep tanks. Two of the three additions caused depressions in the outgo of magnesium from the surface soil, while all three caused augmented losses of magnesium from the subsoil.

All three MgCO₃ additions depressed the calcium outgo from the surface soil and accelerated that from the subsoil. With increased additions, there followed increases in outgo, with a maximum of 34,492 pounds, from the surface soil. The total amounts of magnesium absorbed by the subsoil were practically the same for the 32-ton and 100-ton additions, the two being about twice as great as the amount absorbed by the subsoil from the 8-ton addition.

In harmony with surface soil losses from the CaCO₃ additions, the leachings from 100-mesh limestone were practically the same for the three rates. The absorptions by the subsoil were also independent of rates of additions. The limestone additions showed either depression or but slight accelerations in the outgo of magnesium from the surface soil and liberations from the subsoil.

The losses of calcium from both shallow and deep dolomite tanks increased with increase in rate of treatment. The magnesium leachings, however, failed to show increase with increase in rate of additions. Differing from the other treatments, the dolomite leachings from the deep tanks showed increases of both absorption and passage for both calcium and magnesium.

All magnesite treatments showed a depressive effect upon the outgo of calcium from the surface soil and liberation from the subsoil, together with an augmented effect, independent of rate of addition, upon the magnesium yields from the subsoil.

Wollastonite materially increased the outgo of calcium from the surface soil and through the subsoil and increased the concentration of magnesium in the soil-subsoil leachings. Conversely, serpentine liberated calcium from the deep tank and increased the magnesium concentrations of the deep-tank leachings.

The control subsoil absorbed one-half of the calcium salts leached from the surface, which may account for the increase in its yield of magnesium salts.

Regardless of the concentrations of the several leachings when one base predominated, the subsoil absorbed a part of the content of the surface-soil leachings and permitted passage of concentrations of the predominant base in excess of those from the controls.

As a general tendency, it may be said that where additions gave a preponderance of one alkali-earth, the outgo of the other was depressed in the surface soil and accelerated in the subsoil; i.e., basic exchange was in effect in the subsoil, but "salting out" occurred in the surface soil.

REFERENCES

- (1) BROWN, B. E., AND MACINTIRE, W. H. 1911 The relation of certain water-soluble soil constituents in plots 16-24. *In* Penn. State Col. Agr. Exp. Sta. Ann. Rpt., 1910-1911, p. 105-113.
- (2) LIPMAN, C. B., AND GERICKE, W. F. 1918 Does CaCO_3 or CaSO_4 affect the solubility of the soil's constituents? *In* Univ. Cal. Pub. Agr. Sci., v. 3, no. 10, p. 271.
- (3) LYON, T. L., AND BIZZELL, J. A. 1918 Lysimeter experiments, I. N. Y. (Cornell) Agr. Exp. Sta. Mem. 12.
- (4) LYON, T. L., AND BIZZELL, J. A. 1921 Lysimeter experiments, II. N. Y. (Cornell) Agr. Exp. Sta. Mem. 41.
- (5) MACINTIRE, W. H. 1912 Results of thirty years of liming. *In* Penn. State Col. Agr. Exp. Sta. Ann. Rpt., 1911-1912, p. 73.
- (6) MACINTIRE, W. H. 1919 The carbonation of burnt lime in soils. *In* Soil Sci., v. 7, no. 5, p. 494.
- (7) MACINTIRE, W. H. 1919 The liberation of native soil potassium induced by different calcic and magnesic materials, as measured by lysimeter leachings. *In* Soil Sci., v. 8, no. 5, p. 395.
- (8) MACINTIRE, W. H., SHAW, W. M., AND YOUNG, J. B. 1923 The influence of calcic and magnesic additions upon the outgo of sulfates from a loam soil, as measured by lysimeter leachings over an 8-year period. *In* Soil Sci., v. 16 p. 1-40.
- (9) MACINTIRE, W. H., SHAW, W. M., AND YOUNG, J. B. 1923 Influence of calcic and magnesic additions upon sulfate leachings from soil alone and with additions of ferrous sulfate, pyrite, and sulfur. *In* Soil Sci., v. 16 p. 159-182.
- (10) MACINTIRE, W. H., SHAW, W. M., AND YOUNG, J. B. 1923 A 5-year lysimeter study of the supposed liberation of soil potassium by calcic and magnesic additions. *In* Soil Sci. v. 16, p. 217-223.
- (11) MORSE, F. W. 1923 Relations between calcium carbonate, certain fertilizer chemicals and the soil solution. *In* Soil Sci., v. 15, p. 75-92.

PARTIAL STERILIZATION OF SOIL, MICROBIOLOGICAL ACTIVITIES AND SOIL FERTILITY: III¹

SELMAN A. WAKSMAN AND ROBERT L. STARKEY

New Jersey Agricultural Experiment Stations

Received for publication June 25, 1923

The influence of partial sterilization upon the distribution and activities of microorganisms in the soil has been studied in the previous two papers (11, 12) of this series. It has been shown that partial sterilization depresses the fungi and protozoa and greatly stimulates the development of bacteria. This phenomenon is accompanied by an increase in the ammonia content of the soil, especially in soils rich in organic matter. It remains to be seen, however, how such a modified soil compares with the unmodified soil in its efficiency for decomposing organic substances added to it.

A uniform air-dry Sassafras soil, used in the previous experiments, was placed in 3-kgm. portions, in 6 pots and brought to optimum moisture. After three weeks' incubation, the pots were divided into three groups, two pots in each group. Group 1 was left untreated; 1 per cent of toluene was added to 2, allowed to act for three days, after which the soil was spread out to aid evaporation of the toluene; 0.5 per cent CaO was added to 3, and after 48 hours soil was spread for carbonation to take place. Numbers of microorganisms, nitrate and ammonia content were determined at various intervals, as shown in table 1.

Five days and 20 days after the evaporation of the toluene and carbonization of the CaO, several 100-gm. portions of the soils from the six pots were placed in tumblers and treated as follows: 0.25 gm. of dried blood was added to two tumblers in each group of pots, incubated for 2 weeks, and ammonia and nitrate determined; 30 mgm. of nitrogen as ammonium sulfate and 210 mgm. CaCO₃ were added to two other tumblers, which were then incubated 30 days and ammonia determined. These two methods for the study of nitrification in soil are discussed in detail elsewhere¹ (10); 1 gm. of ground alfalfa meal was added to two other tumblers (containing 200 gm. of soil each) which were then placed in the respirator and the CO₂ evolution determined, as outlined in the previous papers; to two other tumblers in each group of pots, 0.5 gm. of finely cut filter paper was added, the mixture was incubated for 19–21 days and amount of cellulose decomposed determined.² The results are tabulated in tables 2–4.

The treatment of soil with toluene and CaO temporarily injured the nitrifying bacteria, as shown in table 2. This phenomenon has been repeatedly observed by other investigators. In the case of the control soil, 70 per cent

¹ Paper No. 139 of the Journal Series, New Jersey Agricultural Experiment Stations, Department of Soil Chemistry and Bacteriology.

² The authors are indebted to Mr. Heukalikian of this laboratory for making the cellulose determinations. The method used will be described in detail later.

TABLE I
Influence of thioether and CaO upon the microorganisms and their activities in the soil

PERIOD OF INCUBATION	CONTROL POTS						TOLUENE-TREATED POTS						CaO-TREATED POTS							
	+ NH ₃ -ON			NH ₃ -ON			+ NH ₃ -ON			NH ₃ -ON			+ NH ₃ -ON			NH ₃ -ON				
	*A	A	H ₂	Prot.	Prot.	Prot.	*A	A	H ₂	Prot.	Prot.	Prot.	*A	A	H ₂	Prot.	Prot.	Prot.		
days	<i>per cent of thio-sands</i>			<i>mem.</i>			<i>per cent of thio-sands</i>			<i>mem.</i>			<i>per cent of thio-sands</i>			<i>mem.</i>				
Before treatment	11,900	17	40	C	F1	1.44	0.65	12,800	17	C	F1	1.44	0.82	14,200	20	42	C	F1	1.44	0.90
0	15,800	17	42	C	F1	1.54	0.70	6,300	13	0.33	0	2.28	0.78	8,960	5	14	C	F1	2.48	0.55
5	11,700	18	41	0.74	2.30	5,400	9	0.33	1.75	1.03	35,000	3	25	1.68	0.53
15	9,400	23	28	C Am	F1	0.84	4.55	60,200	2	1.3	0	2.03	1.65	46,000	1	7.1	C	F1	1.47	0.54
23	10,600	23	25.3	C Am	F1	0.94	2.85	111,300	1	10.1	Am F1	2.44	1.05	42,000	2	12.9	C Am	F1	1.42	0.70
40	11,070	20	18	1.12	3.60	102,000	3	43.3	4.18	1.10	70,000	1	9.3	1.63	3.30
70	11,200	19	28.5	1.44	4.55	38,000	6	49.2	2.88	2.80	21,500	3	15	2.02	4.95
90	10,150	25	24.5	C Am	F1	0.87	4.70	42,200	8	56	C Am F1	2.31	4.05	18,000	3	7	C Am	F1	0.65	5.80

* B = bacteria, A = actinomycetes, F = fungi, C = ciliates, Am = amoebae, and Fl = flagellates.

of the soluble nitrogen, as a result of the decomposition of dried blood, was in the form of nitrate, while in the case of the toluene and CaO treated soil, there was no more nitrate than in the original soil, i.e., the dried blood had been transformed into ammonia, but none of this was nitrified. The same was true in the case of nitrification of the ammonium sulfate. The toluene treated soil was more efficient in decomposing dried blood than the CaO treated soil, but less efficient than the control soil. This was due to the difference in the active flora. The control soil, rich in fungi, decomposed the dried blood rapidly into ammonia and a part of the ammonia was oxidized into nitrates by the efficient nitrifying flora. In the toluene-treated soil, the fungi were suppressed, while the bacterial flora was modified; the actinomycetes were, however, only slightly affected. As shown in the previous paper, actinomycetes can develop very rapidly in toluene-treated soils,

TABLE 2
*Nitrifying capacity of toluene and CaO treated soils**

AGE OF TREATED SOIL	TREATMENT OF SOIL	FROM DRIED BLOOD		$\text{NO}_3 - \text{N}$ FROM $(\text{NH}_4)_2\text{SO}_4 + \text{CaCO}_3$
		$\text{NH}_3 - \text{N}$	$\text{NO}_3 - \text{N}$	
days		mgm.	mgm.	mgm.
5	Control	7.8	18.7	30.9
5	Toluene	20.6	2.1	2.0
5	CaO	16.2	0.2	0.5
15	Control	5.4	23.2	
15	Toluene	20.8	2.3	
15	CaO		2.7	

* Incubation of tumblers: 14 days for dried blood, 30 days for the ammonium sulfate.

especially those rich in organic matter; this is the reason why the toluene-treated soil is less efficient in decomposing dried blood than the control soil but more efficient than the CaO treated soil. The bacterial numbers for the CaO treated soil were 35 millions in 5 days and 46 millions in 15 days, or 3-4 times as high as in the control soil; the actinomycetes, however, were depressed almost completely and the fungi to some extent. This soil with its high bacterial population was least capable of decomposing the dried blood. This was due, in addition to the relative inactivity of the fungi and actinomycetes, to the reaction of the soil which was pH 8+. A large bacterial population, therefore, may not necessarily indicate an active flora. This is brought out even with greater emphasis in tables 3 and 4.

When 0.5 per cent of alfalfa meal is added to the variously treated soils, different groups of organisms are stimulated. The fungi develop rapidly in the control soil, the bacteria and actinomycetes in the toluene-treated soil, and the bacteria in the CaO-treated soil. The results give a very interesting demonstration of the relative rôle of fungi, actinomycetes and bacteria in the decomposition of organic matter in the soil, as indicated by the evolution

of carbon dioxide. The control soil in which the fungi predominated was most efficient, the toluene-treated soil came next and finally the CaO-treated soil. The most efficient soil happened to be the one in which the bacterial population was least to start with, but which contained a vigorous fungous

TABLE 3

*Influence of alfalfa meal upon the microbiological activities in toluene and CaO treated soils**

AGE OF TREATED SOIL	TREATMENT OF SOIL	CO ₂	NH ₄ †	NO ₃	BACTERIA	ACTINOMY- CETES	FUNGI	REACTION
days		mgm.	mgm.	mgm.	thousands	thousands	thousands	pH
5	Control	333.59	1.01	3.30	65,200	16,500	240	6.6
5	Toluene	292.98	2.95	0.35	181,000	50,000	169	6.8
5	CaO	273.28	1.01	3.60	224,000	5,500	137	7.6
15	Control	675.84						
15	Toluene	614.64						
15	CaO	608.00						

* For those soils which were analyzed 5 days after treatment 0.5 gm. of alfalfa meal was applied per 100 gm. of soil and incubated for 7 days; for the remainder 1 gm. of alfalfa meal was applied per 200 gm. of soil and incubated for 9 days.

† The amounts of ammonia and nitrate as well as numbers of microorganisms in the original treated soils, from which the samples of soil were taken for this experiment, are given in table 1 under the corresponding dates.

TABLE 4
*Cellulose-decomposing capacity of toluene and CaO treated soils**

AGE OF TREATED SOIL	TREATMENT OF SOIL	CELLULOSE DECOMPOSED	BACTERIA	ACTINOMYCETES
days		per cent	thousands	thousands
5	Control	38.4	25,000	1,200
5	Toluene	32.4	30,900	11,200
5	CaO	17.6	106,000	3,000
15	Control	59.4		
15	Toluene	50.8		
15	CaO	50.4		

* For each 100 gm. of soil 0.5 gm. of cellulose was used. The soils analyzed 5 days after treatment were incubated for 19 days; the remainder, 30 days.

flora. In the control soil the bacteria developed least and the fungi, most. In the toluene-treated soils, the bacteria developed to much larger numbers than in the control soil, but to a somewhat smaller extent than in the CaO-treated soil; fungi, however, developed to a more limited extent than in the control, although to a somewhat greater extent than in the CaO-treated soil; the actinomycetes developed most abundantly in the toluene-treated soil and it is these organisms which are partly responsible for the decomposition of

the organic matter in the toluene soil, above that of the CaO-treated soil. The natural conclusion from this experiment is that a large bacterial flora, when the fungi and actinomycetes are not considered, need not necessarily indicate a flora efficient in decomposing organic matter. As to the protozoa, they were present in great abundance in the control soil, entirely absent in the toluene-treated soil and present in limited numbers (chiefly flagellates) in the CaO-treated soil. No correlation whatsoever was found between the presence or absence of protozoa and the efficiency of a soil flora in decomposing organic matter.

Table 4 shows the efficiency of the flora in the three soils in decomposing cellulose, as indicated by the actual amount of cellulose which disappeared in the soil. The results for the soil used 5 days after treatment are more important, since the tumblers were incubated only 19 days. The samples taken 15 days after treatment, to which cellulose has been added were incubated for 30 days. The fungi developed at first abundantly in the tumblers containing the control soil, but not in the toluene- and CaO-treated soils. However, after a week or so, the soils became heavily reinoculated and all showed an equally abundant fungous flora. This accounts for the comparatively large amount of cellulose decomposed in the case of the soils taken 15 days after treatment, especially in the toluene- and CaO-treated soils. The same phenomena are brought to light here as in the case of the CO₂-evolution study. In the control soil, the bacteria developed to a limited extent, increasing from 11,700,000 to 25,000,000, the actinomycetes hardly developed at all, while the fungi increased in great abundance (to over 200,000 per gram). It is this soil which decomposed cellulose most efficiently. In the toluene-treated soil, the bacteria increased from 5,400,000 to 30,900,000, while the actinomycetes increased to 10 times the number of the control soil; the fungi were low at first, but, due to the long period of incubation, they also finally increased to large numbers. In the CaO-treated soil, the bacteria have reached the highest numbers, while the actinomycetes increased slowly and the fungi only at the latter part of the incubation period. It is not so much the high number of bacteria which is responsible for the decomposition of cellulose in the soil as the high number of fungi and actinomycetes.

It remains to be seen how the various organisms developing in the soil can be made to liberate the nitrogen that they have assimilated in their bodies.

Störmer (8), Stoklasa (7) and others have claimed that the stimulating action of the disinfectants upon bacterial activities and ammonia accumulation is due to the destruction of large soil organisms, such as worms, insects, nematodes, algae, fungi, protozoa as well as bacteria; these are then decomposed by the surviving bacteria with the result that a rapid bacterial development takes place accompanied by an abundant ammonia formation. As a matter of fact, Störmer suggested that, since the total increase in ammonia nitrogen in the treated over the untreated soil is not more than 3-4 mgm.

of nitrogen per 100 gm. of soil, this quantity can readily be derived from the decomposed organisms. Hiltner (4) used a logical process of reasoning in demonstrating the destruction of fungi and actinomycetes by volatile anti-septics. When straw is added to the soil, the available nitrogen is stored away by the microorganisms to the detriment of the higher plants. When the soil is treated with CS₂ during or after the addition of straw, the injurious influence is not observed. This was explained by the fact that, in the case of straw fertilization, the soil nitrogen is stored away chiefly by fungi and actinomycetes. The disinfectant, in destroying the fungi and actinomycetes, prevents the storing away of the soil nitrogen, which thus becomes available for higher plants. These considerations were based merely on theoretical considerations. No actual facts have been submitted to demonstrate whether they are true or not. According to this theory, the stimulating effect of disinfectants and heat upon bacterial development is due to the destruction of protozoa, with the result that their dead cells serve as an available source of energy for the bacteria, while according to the protozoan theory the beneficial influence of disinfectants is due to the destruction of protozoa which otherwise check the development of bacteria.

The results that we have previously reported have shown that there is no correlation (except in one or two instances) between the suppression and later development of protozoa and bacterial development. There is, however, a certain correlation between the development of bacteria and of filamentous fungi in the soil. The authors do not claim that the development of fungi in the soil has a depressive action upon the development of bacteria, but merely that the numbers of bacteria are governed by the balance of microorganisms in the soil, including the fungi and actinomycetes and perhaps also the protozoa. If the assumption of Störmer (8), Stoklasa (7) and others could actually be demonstrated, namely that the influence of disinfectants in destroying a large part of the microbial population of the soil makes their bodies available as a source of energy for the bacteria, it would throw a great deal of light upon the subject under consideration. Not that it would solve the problem, but it would be merely one more link in the chain explaining the very complex phenomenon resulting from the partial sterilization of soil. To demonstrate the rôle of disinfectants in the making of dead bodies of soil microorganisms readily available sources of energy for bacteria, those microorganisms would have to be introduced in sufficient quantities in the soil, so as to allow measurable increases in bacterial development to take place and yield measurable quantities of ammonia. Were these added in the form of fully developed cells grown on artificial culture media, a good deal of the material might consist of dead autolized cells rich in proteins and minerals, or nutrients adhering from the artificial medium; this would have created purely artificial conditions. The problem is to bring about a rapid increase of one or more groups of microorganisms in the soil, without modifying the physical and otherwise microbiological condition of the soil and especially without de-

stroying, injuring or otherwise modifying the activities of protozoa and without adding fresh protein material to the soil. The filamentous fungi were selected as a group of organisms to be stimulated, for various reasons:

1. We know more about the specific metabolism of these organisms than about many other soil microorganisms 2. They grow rapidly. 3. Methods have been developed (9) for at least an approximate determination of their abundance in the soil. 4. Our previous results have shown us that the abundance of fungi in the soil is appreciably affected by treatment of soil with disinfectants. 5. They do not enter into the system "protozoa-bacteria" as developed by Russell and associates. 6. They can be handled, studied, identified in the laboratory and controlled in the soil more readily than worms, nematodes, insects, algae and protozoa.

Studies now being carried on in our laboratory and the data reported previously by other investigators on the influence of cellulose upon the activities of soil microorganisms as well as on the specific groups of organisms concerned in the decomposition of cellulose in the soil, demonstrated that the addition of pure cellulose to the soil greatly stimulates the development of fungi and that the fungi use up all the available nitrogen compounds in the soil, in the presence of sufficient cellulose as a source of energy, and convert it into fungus protoplasm. The growth of fungi may be so abundant as a result of addition of cellulose to the soil, especially if the soil is rich in nitrates, ammonium salts and other available nitrogen compounds, that it is difficult to accurately count the numbers of bacteria and actinomycetes by the common plate method using synthetic media. This may even be the case with high dilutions. As a result of adding cellulose to ordinary soil, the bacteria and especially the actinomycetes are also stimulated but to a lesser extent than the fungi.

This phenomenon has been utilized for increasing the fungus content of the soil. The cellulose used was pure, ash-free filter paper, cut up into very small pieces and well mixed with the soil. Four 1-kgsm. portions of the same air-dry soil used in the previous experiments were placed in 4 glazed earthenware pots and the optimum amount of moisture added (20 per cent). One per cent of cellulose was well mixed in with the soil in two of the pots before the moisture was added. The pots were covered with glass plates and placed in the incubator. No nitrates or nitrogen salts were added, since it was known from previous work with the particular soil that nitrates will accumulate very rapidly when the soil is kept under optimum moisture and temperature conditions. However, since all the nitrate had disappeared in the cellulose pots after 8 days' incubation (see table 5), 500 mgm. of NaNO_3 (82 mgm. N) was added on the twentieth day of incubation to each of the four pots so as to allow as complete a transformation of the cellulose into fungus mycelium as possible. The addition of a large amount of nitrate to the cellulose-free soils, already rich in nitrate led to a partial reduction of the nitrate to ammonia; in the cellulose pots, however, no such reduction took place. Twenty days after the addition of nitrate, the soils from the four pots were transferred to glass stoppered bottles, 2 per cent of toluene was

added to each and allowed to act for 72 hours. At the end of that period of time, the soils were spread out for the toluene to evaporate and returned to the original pots, brought up to moisture, covered and placed in the incubator. Determinations of numbers of microorganisms, ammonia and nitrate content are shown in table 5.

Treatment of the soils with toluene brought about first a decrease, then a decided increase in the number of bacteria both in the soil to which no cellulose has previously been added and to the cellulose-treated soils, the increase

TABLE 5
Influence of cellulose upon the growth and activities of microorganisms in the soil

PERIOD OF INCUBA- TION	NO CELLULOSE ADDED TO SOIL						1 PER CENT OF CELLULOSE ADDED TO SOIL					
				N per 100 gm. soil						N per 100 gm. soil		
	B + A per gm. soil*	A	Fungi per gm. soil	as NH ₃	as NO ₃	Total	B + A per gm. soil	A	Fungi per gm. soil	as NH ₃	as NO ₃	Total
day:	thou- sands	per cent of B+A	thou- sands	mgm.	mgm.	mgm.	thou- sands	per cent of B+A	thou- sands	mgm.	mgm.	mgm.
8†	33,800	10.0	48.0	10.8	41,400	9	458	Trace	0
34	19,000	16.0	49.5	8.69	17.8	26.49	40,000	?	1315	1.80	6.1	7.90
43	16,400	22.0	12.0	8.30	17.9	26.20	22,200	39	63	2.30	8.8	11.10
52	25,400	8.7	13.5	9.71	17.2	26.91	64,700	5	140	6.84	4.5	11.34
69	62,500	7.0	17.5	11.52	18.2	29.72	95,500	16	162	9.36	3.9	13.26
98	46,500	6.0	142.0	12.67	15.7	28.37	78,500	15	197	7.75	8.8	16.55
118	38,000	7.0	33.0	11.52	15.8	27.32	77,000	20	225	0.95	15.5	16.45

* In this table, the term "Soil" means moist soil just as it was removed from the culture pots.

† Treatments consisted of mixing 1 per cent of cellulose with dry soil and adding 20 per cent of water just before the period of incubation. After 20 days of incubation 82 mgm. of nitrate nitrogen was added to the soil in each pot. Twenty days after the addition of the nitrate, the soils were treated with toluene which was evaporated three days later.

being greater in the case of the latter. The fungi were reduced by the use of toluene and then increased greatly, more so in the cellulose treated soils. The total soluble nitrogen increased only slightly in the soils to which no cellulose has been added, while in the cellulose-treated soils there was a steady increase; in 78 days after toluene-treatment the soluble nitrogen in the former increased from 26.49 to 27.32 mgm. per 100 gm. of soil while, in the cellulose-treated soils, it increased from 7.90 to 16.45 mgm. This is due to the gradual decomposition of the fungi and other microorganisms which have originally stored away the nitrate in the form of microbial proteins using the cellulose as a source of energy.

DISCUSSION

To be able to understand the change in the growth and activities of the different groups of microorganisms in the soil, as a result of partial steriliza-

tion, we must clearly understand the differences in the metabolism of these groups of microorganisms, especially the nitrogen and carbon (energy) metabolism; we must also in some cases differentiate between the amount of carbon used by the organisms for structural and functional purposes and the amount of nitrogen needed for synthesis of microbial protoplasm and liberated as a waste product in the form of ammonia. In other words, the carbon and nitrogen of each representative group of soil organisms should be kept in mind when we attempt to understand and interpret the changes in the carbon and nitrogen cycles in the soil.

The three groups of soil microorganisms, which take an active part in the transformation of carbon and nitrogen in the soil are the fungi, actinomycetes, and bacteria. These are the organisms that develop on the plates and which we are thus able to count. There are other microorganisms in the soil which undoubtedly take an active part in the carbon and nitrogen cycles, especially the protozoa, and possibly the nematodes, rotifers and worms. By consuming living microorganisms or dead organic matter, the latter bring about certain changes in the chemical condition of the carbon and nitrogen in the soil. However, our knowledge on the metabolism of these organisms in the soil is still insufficient to warrant any generalizations. What we do know leads us to think that there is at least no appreciable increase or decrease in the total amount of carbon and nitrogen in the soil, as a result of their activities, although there may be a change in the physical and chemical condition of the soil. The algae may also take a part in increasing the carbon and nitrogen content of the soil, but their contribution to the chemical changes in the soil is still not definitely known. Still less do we know about the activities of the ultra microscopic and filterable organisms that no doubt exist in the soil.

It remains, therefore, for us to keep in mind the metabolism of the fungi, actinomycetes and bacteria—the three leading groups of microorganisms which take an active part in the transformations of carbon and nitrogen in the soil. Out of these three groups, the metabolism of the bacteria is the most complex, since it differs with the different representatives of the group. Those bacteria that develop on the plate are heterotrophic forms, so that the important nitrifying, sulfur oxidizing and other autotrophic bacteria are left out; conditions are aerobic, so that the obligate anaerobes are left out; most of the nitrogen-fixing organisms and probably many cellulose decomposing forms as well as others do not appear. But even the heterotrophic forms developing on the plate can be readily divided into two distinct groups: the spore forming and the non-spore forming types. The former grow rapidly, are usually strongly proteolytic, decompose readily starches and other carbohydrates. The non-spore forming bacteria grow slowly, either liquefy gelatin or do not liquefy it at all, and do not attack starches and other carbohydrates readily. Of the colonies developing on the plate, outside of the fungi, the actinomycetes occupy 15 to 35 per cent, the spore-forming bacteria 5-10 per cent and the non-spore forming bacteria 55-70 per cent. There is evi-

dence to believe [Conn (1, 2)] that of the two groups of bacteria, the non-spore forming group is not only the most predominant but the most active in the soil. Of special interest is the energy metabolism of these organisms; they seem to use proteins much more readily than carbohydrates(?), thus liberating comparatively large quantities of ammonia. It is, therefore, quite natural that the great majority of media recommended for the cultivation of bacteria should contain a protein in one form or another, while in the case of fungi and actinomycetes, a carbohydrate is usually offered as a source of energy. The following paragraphs deal with the carbon and nitrogen metabolism of the organisms developing on the plate.

Fungi

Fungi prefer carbohydrates as sources of energy although they can also use proteins; of the carbohydrates, many can utilize celluloses, hemicelluloses and starches, others only the derivatives of those products. Nitrogen can be obtained from nitrates, ammonium salts, amino acids and proteins. They grow rapidly and may use up to 50 per cent of the carbon assimilated for the synthesis of their protoplasm. Although the nitrogen content of fungus mycelium varies within 3.5 to 7.0 per cent, large quantities of nitrogen will be transformed into fungus protein due to the abundant assimilation of carbon. When an organic substance containing a small amount of nitrogen (less than 1.5 per cent) is acted upon by fungi, the organisms may decompose it very rapidly, liberating large amounts of CO_2 , but, in view of the large amount of carbon assimilated, an additional source of nitrogen will be required; this additional need for nitrogen increases with a decrease in the nitrogen content of the energy bearing material.

Partial sterilization of soil practically eliminates certain groups of fungi from the soil and greatly reduces the number of all fungi. It requires some time, depending upon treatment and content of organic matter in the soil, before the fungi become reestablished. Their rapid multiplication then depends upon the amount of energy available. If that is at all extensive, the fungi multiply rapidly, especially when reinoculated. Their rapid development will result in two phenomena: (a) a competition with the heterotrophic bacteria for the available energy, which will lead to a diminution of the latter and (b) a stop to a further increase of the soluble nitrogen in the soil. This action of fungi upon bacterial multiplication and activities is indicated by a number of statements in the literature, of which we need only cite that of Scherpe (6).

Scherpe (6) found in 1909 that the treatment of soil with CS_2 decidedly stimulated the development of fungi, which influences the nitrogen transformation in the soil by fixing in the mycelium the easily assimilable nitrogen compounds in the soil or the ammonia liberated by the bacteria. Scherpe, therefore, suggested that fungi may play an active part in the group of phenomena resulting from treatment of soil with CS_2 . It is important to note that

some fungi actually secrete substances toxic to the development of bacteria, as shown by Nadson and Zolkiewicz (5) for *Spicaria* and as observed repeatedly by the authors in the case of certain species of *Rhizopus*, whose development on the plate is sufficient to repress almost completely the development of the bacteria.

Actinomycetes

Actinomycetes are not any more appreciably affected by partial sterilization than the bacteria developing on the plate. In other words the ratio of actinomycetes to the total number of bacteria developing on the plate may remain the same, may slightly diminish or may even increase, as a result of partial sterilization. While the fungi are practically eliminated, the actinomycetes are diminished only slightly in numbers. However, their multiplication is very slow and when the bacteria begin to multiply rapidly as a result of partial sterilization, the numbers of actinomycetes may remain stationary, while their ratio rapidly diminishes, in proportion to the increase in bacterial numbers. When available energy like cellulose is added, the actinomycetes begin to multiply rapidly. They can use as sources of energy celluloses and other carbohydrates as well as proteins. Ammonium salts, nitrates, amino acids and proteins can be used as nitrogen sources. In their carbon-nitrogen metabolism they stand between the aerobic bacteria and the fungi, having a higher nitrogen content than fungi and making a much less abundant growth. Their activities would tend to bring about an increase in the available nitrogen in the soil rather than a decrease, unless an excess of energy material, free from nitrogen, is available. These organisms will therefore consume a smaller amount of nitrogen with the same amount of cellulose decomposed; they will liberate a greater amount of ammonia from proteins than fungi, for the same amount of protein decomposed.

The development of actinomycetes probably does not act as a direct repressive agent of bacteria even though the ratio of actinomycetes increases when the bacteria begin to diminish. The latter may possibly be due not so much to a direct increase of numbers of actinomycetes, but to a relatively greater decrease of bacteria.

Treatment of certain soils with toluene or CS₂ may make them more favorable media for the development of actinomycetes, as shown in the previous papers (11, 12).

Certain actinomycetes produce substances toxic to bacteria, as shown by Greig-Smith (3) and as often observed in our own work, when around an actinomycetes colony upon a plate, a zone is found free from fungus and bacterial growth.

Spore-bearing aerobic bacteria

These organisms decompose chiefly soil proteins, starches and simpler carbohydrates. One or two species of the anaerobic forms can also decom-

pose celluloses. These organisms make a more limited amount of growth than the fungi and actinomycetes, but their bodies are richer in nitrogen, containing 6 to 12 per cent (usually 10 per cent) of this element. In other words, the nitrogen content of bacteria is twice as high as that of fungi. They are also less economical in their utilization of carbon than fungi.

Non-spore bearing bacteria

These organisms readily utilize proteins and other carbon-nitrogen compounds as sources of energy. Some can also decompose celluloses and other carbohydrates. A great many of these organisms (developing on the common plate) thrive, however, with celluloses, starches and other carbohydrates as sources of energy to a lesser extent than the spore-bearing bacteria and much less so than the fungi and actinomycetes. Their nitrogen content is about 10 per cent, while they utilize carbon even less economically than the spore-bearing bacteria. It is this group which contains the majority of organisms developing on the plate and it is this group which is favorably affected by partial sterilization of soil.

When soil is treated with heat and antiseptics, the organic matter is modified and made more readily available. The fungi are destroyed. The nematodes, protozoa, insects, worms are also destroyed and leave an abundant supply of relatively available material. The non-spore bearing bacteria are the first to become active and to multiply rapidly. Masses of these organisms are easily broken down in preparing the soil dilution and show up readily on the plate. They decompose proteins and other nitrogenous substances readily as a source of carbon. Only a small amount of the carbon is assimilated and converted into microbial proteins, and *ipse facto* only a small amount of the nitrogen is assimilated. Most of the carbon is liberated as CO₂ and the nitrogen as ammonia; in the absence of nitrifying bacteria, the latter is left in the soil as such. When the partially sterilized soil is reinoculated with fresh soil, various other organisms, and particularly the fungi are reintroduced. These organisms find the treated soil a favorable medium for their development.

Our knowledge of the kinds and activities of soil microorganisms is still insufficient; we know very little about the various antagonistic and associative influences between the various groups of soil microorganisms, especially between the bacteria on the one hand and actinomycetes, fungi and protozoa of the other. It is not a question of one group of organisms destroying another group, although this may take place under exceptional circumstances, but it is chiefly a question of competition for available nutrients especially energy, or of one group developing more readily in the absence of the other groups. Under normal conditions very little readily available nutrients, especially energy sources, are present in the soil at any one time. The introduction

of available energy combined with nitrogen and minerals, as in the case of alfalfa hay, brings about a stimulus to microbial activities similar to partial sterilization. Some microorganisms liberate available nitrogen compounds in the soil, others transform them into microbial protein, in the presence of available energy; a certain balance or equilibrium is established between these phenomena in ordinary soils. Partial sterilization changes this equilibrium.

The effect of partial sterilization of soil is a resultant of the sum total of the changes in the physical and chemical condition of the soil on the one hand and of the modification of the biological flora on the other. Treatment with antiseptics, heat, calcium oxide, air drying etc. affect the first and modify the second and the resultant phenomenon is an increase in the number of bacteria and ammonia content of the soil.

SUMMARY

1. Partial sterilization of soil brings about a chemical change in the organic matter of the soil, making it more available as a source of energy for micro-organisms. This is indicated by (a) the ammonia formation (even if only a small amount) in the process of sterilizing the soil by heat or disinfectants; (b) by the fact that the curve of CO₂-evolution in partially sterilized soil is similar to that obtained when a small amount of undecomposed organic matter is added to unsterilized soil; (c) by the fact that soils rich in organic matter allow a greater accumulation of ammonia and nitrates, as a result of partial sterilization, than soils poor in organic matter, independent of the flora and fauna; (d) partially sterilized soil with a much greater bacterial flora is no more efficient in decomposing nitrogenous and non-nitrogenous organic substances added to it.

2. A large proportion of the soil fungi are killed as a result of partial sterilization. This dead material with the bodies of destroyed protozoa and other soil microorganisms still further increases the amount of energy made available in the soil.

3. The rapid increase in the numbers of microorganisms in the soil is at the expense of the organic matter made available. This is further confirmed by the fact that the course of development of fungi results in a curve somewhat similar to that given by the bacteria, although the rise in the curve may take place at a later date. The numbers of fungi, however, may not indicate the period of maximum activity which may have been passed already. Large numbers of fungi, shown by the plate method, may be due to abundance of spores. Where active growth of fungi takes place, due to available nutrients, spore formation may be greatly delayed. The vegetative mycelium, however extensive, may show much smaller numbers than when spore formation occurs.

4. The carbon and nitrogen are present in the soil in a certain proportion, depending upon the physical and chemical condition of the soil; when the

carbon compounds are decomposed as sources of energy by the bacteria and actinomycetes some of the nitrogen is left as a waste product. The carbon-nitrogen content of the soil and of the bodies of the bacteria, actinomycetes and fungi combined with the economic utilization of the carbon by these three groups of organisms, explain why the development of the first two groups of organisms will bring about the liberation of nitrogen from the soil organic matter to a greater extent than the development of the fungi.

5. The actual amount of ammonia formed in partially sterilized soil is determined not by the numbers of bacteria and fungi developing in the soil but by the abundance of organic matter. The course of development of numbers of bacteria in the soil seems to be influenced by the course of development of the fungi. The course of development of actinomycetes depends upon the method used in bringing about the partial sterilization of the soil as well as by the organic matter content of the soil.

6. The protozoa are suppressed in partially sterilized soil, but become active again long before the bacterial numbers drop down very markedly.

7. The more rapid the rise in bacterial numbers and the greater the maximum, the sooner will the fall set in. This is exactly true of the numbers of fungi. These phenomena are results of the amount of available plant food in the soil.

8. The phenomena observed as a result of partial sterilization of soil, namely the rise of bacterial numbers and ammonia accumulation are explained by (a) the change in the physical condition of the soil, especially the soil colloids; (b) the change in chemical condition, especially modification of soil organic matter, making it more readily available; (c) the destruction of a large number of soil microorganisms, especially the fungi and protozoa, making their bodies available as sources of energy for the surviving microorganisms; (d) the change in balance of the microbiological flora of the soil (all of these favor greatly the development of the bacteria); and (e) the fact that bacteria use organic nitrogenous substances (as well as other carbon compounds) very uneconomically as sources of energy and liberate a great deal of ammonia as well as phosphates and other minerals stored away in the soil organic matter as waste products.

9. These results apply to normal soils. It is possible that under certain conditions other phenomena become controlling factors. We need only mention soils infested with fungi causing plant diseases or sewage farming and greenhouse soils, where protozoa may become controlling factors.

REFERENCES

- (1) BRIGHT, J. W., AND CONN, H. J. 1919 Ammonification of manure in soil. N. Y. Agr. Exp. Sta. Tech. Bul. 67.
- (2) CONN, H. J., AND COLLISON, R. C. 1922 Fermentation and preservation of manure: I. A study of certain bacteria involved in the ammonification of manure. N. Y. Agr. Exp. Sta. Bul. 494.

- (3) GREIG-SMITH, R. 1917 The action of certain microorganisms upon the numbers of bacteria in the soil. *In Proc. Lin. Soc. N. S. Wales*, v. 42, p. 162-166.
- (4) HILTNER, L. 1908 Über neuere Ergebnisse und Probleme auf dem Gebiete der landwirtschaftlichen Bakteriologie. *In Jahrest. Angew. Bot.* v. 5, p. 200-222.
- (5) NADSON, G. A., AND ZOLKIEWICZ, A. I. 1922 *Spicaria purpurogenes* n. sp. On the antagonism of microorganisms. (Russian.) *Bul. Jard. Bot. Repub. Russe.*, v. 21, Add. 1, p. 1-18.
- (6) SCHERPE, R. 1909 Über den Einfluss des Schwefelkohlenstoffs auf die Stickstoffumsetzungsvorgänge im Boden. *In Arb. Biol. Abt. Land. u. Forstw. K. Gandhtsamt.*, no. 3, p. 353-428.
- (7) STOCKLASA, J. 1911 Biochemischer Kreislauf des Phosphat-Ions im Boden. *In Centbl. Bakt. (etc.), Abt. 2*, v. 29, p. 185.
- (8) STÖRMER, K. 1908 Über die Wirkung des Schwefelkohlenstoffs und ähnlicher Stoffe auf den Boden. *In Centbl. Bakt. (etc.), Abt. 2*, v. 20, p. 282-286.
- (9) WAKSMAN, S. A. 1923 Microbiological analysis of soil as an index of soil fertility. IV. Ammonia accumulation (ammonification). *In Soil Sci.* v. 15, p. 49-65.
- (10) WAKSMAN, S. A. 1923 Microbiological analysis of soils as an index of soil fertility. V. Methods for the study of nitrification. *In Soil Sci.*, v. 15, p. 241-260.
- (11) WAKSMAN, S. A., AND STARKEY, R. L. 1923 Partial sterilization of soil, microbiological activities and soil fertility. I. *In Soil Sci.* v. 16, p. 137-158.
- (12) WAKSMAN, S. A., AND STARKEY, R. L. 1923 Partial sterilization of soil, microbiological activities and soil fertility. II. *In Soil Sci.* v. 16, p. 247-268.

CONVENIENT SUPPORTS FOR PLANTS IN POT OR WATER CULTURE EXPERIMENTS

J. S. McHARGUE

Kentucky Agricultural Experiment Station

Received for publication July 1, 1923

It is frequently necessary to provide some means for supporting plants that are to be grown for some time in either pot or water culture experiments. It is desirable that such supports be light, substantial, easily attached and interfere as little as possible in handling the pots. For our own convenience two methods have been devised. Plate 1 shows each of the two methods described. The sticks on the jar on the left are inserted into metal sockets each made from a piece of galvanized sheet iron two inches square. These are made by hand as indicated in figure 1.

The middle jar in plate 1 shows plants during their growth in water cultures; the pot on the right shows the perforated earthenware cover which holds the plants and the wood supports. The cover fits over the mouth of the one-gallon earthenware jar and the plants are held at the proper place in the cover by means of plugs of cotton. The roots are submerged in the nutrient solution contained in the jar. This arrangement makes it easy to lift off the cover carrying the plants when changing the culture solution. Three of the four holes for the wood supports are shown in the outer edge of the cover. The holes within the rim are about $\frac{1}{4}$ inch in diameter.

The earthenware covers were made for us by the Maurice A. Knight Company and have proved to be very satisfactory for growing plants in water cultures. Similar covers made of wood and water-proofed with paraffin proved to be unsatisfactory because of their lightness, warping, cracking and affording a foot-hold for the growth of molds. The earthenware cover eliminates these troubles.

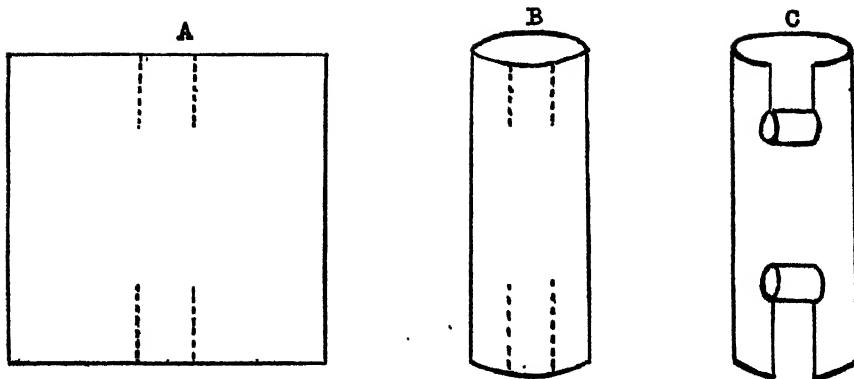
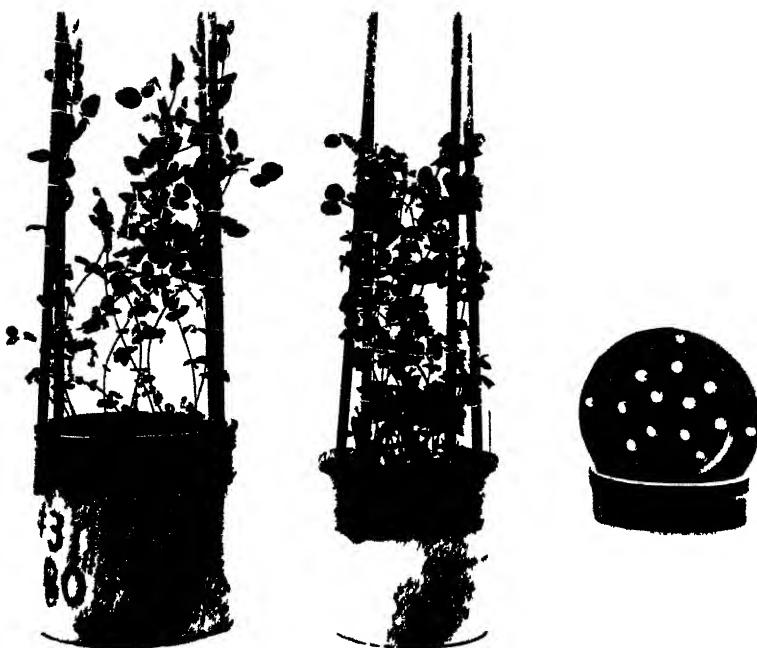


FIG. 1. METHOD OF MAKING METAL SOCKETS FOR PROPS

At A the metal square has been cut along the dotted lines, and at B the square has been bent into the form of a cylinder. This is done by bending one edge over the other and hammering over an iron rod about $\frac{1}{2}$ inch in diameter until a cylinder is formed. At C the small tongues have been bent over a no. 4 nail with a pair of pliers. Four of the sockets are then strung on two pieces of baling wire at equal distances apart on the wires and attached to the top of the jar by twisting the ends of the same piece of wire together around the jar until tight. Rods of wood are placed in the metal sockets and twine stretched from one support to another at the proper height, as may be needed during the growth of the plants to keep them in an upright position.

SUPPORT FOR PLANTS IN POT OR WITH CULTURALS
S CIRCLE

PLATE 1



A NEW APPARATUS FOR MECHANICAL ANALYSIS OF SOILS

HARLAN W. JOHNSON

Iowa Agricultural Experiment Station

Received for publication July 1, 1923

The study of soil physics, very popular some years ago, seems to be reviving. Chemical and bacteriological studies of soils have not given entirely satisfactory explanations of the various factors which affect soil fertility. The advance of physical chemistry has added many new methods and implements to be used in this work and is giving a greater insight into the phenomena that must be investigated.

The author wishes to present a preliminary description of an apparatus devised for obtaining a better conception of the physical constituents of the soil. It has always been recognized that the proportions of the soil particles of various sizes were the controlling factors in determining soil characteristics and various means of making mechanical analyses have been devised for determining these proportions.

For some time these methods have been recognized as inadequate in that they do not give a sufficiently detailed picture of the soils. The separation, which is necessary, into fractions of arbitrarily fixed diameters is not satisfactory because the soil is made up of particles varying in size continuously and not by steps. The picture presented by such an analysis is not correct.

Recently Sven Oden (1) has described an apparatus which much more nearly indicates the actual mechanical composition of the soil. By suspending the soil particles in water and allowing them to settle upon the pan of a balance, recording automatically the time required for a definite weight of particles to settle, he obtains by mathematical calculations a distribution curve.

The apparatus here described is patterned somewhat after Oden's balance. It goes farther than his, however, in that it draws the distribution curve itself, thereby eliminating the complicated calculations necessary with Oden's balance. The illustration shows the balance diagrammatically. The instrument as now made has not as yet been corrected or even calibrated. It is not the intention of the author that it should be constructed as delicately as Oden's apparatus since it does not seem probable that very minor differences in texture are of significance in soils. The apparatus has been tested only experimentally as yet. It has been found that some features should be changed. It seems particularly necessary that the recording drum revolve much faster. The balance may need to be made somewhat more sensitive in order than smaller quantities of soil may be used.

The principal feature of the apparatus is the recording arrangement. If the balance beam recorded its movements by marking upon the moving chart, the necessary friction would reduce its sensitivity. This was avoided by making the record electrically. A momentary contact at regular intervals causes a spark to jump from the point at the end of the beam to the revolving cylinder, passing through the record chart and burning a small hole. Since the electrical connection is made at the base of the balance column and the cur-

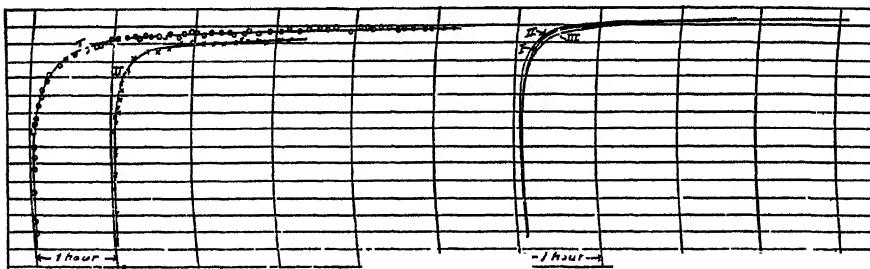


FIG. 1. CURVES SHOWING ACTUAL POINTS AS LOCATED BY BALANCE

FIG. 2. CURVES OF THREE SOILS NOT DEFLOCCULATED

- I. Deflocculated
- II. Not deflocculated

- I. Webster silty clay loam
- II. Carrington loam
- III. Lintonia silt loam

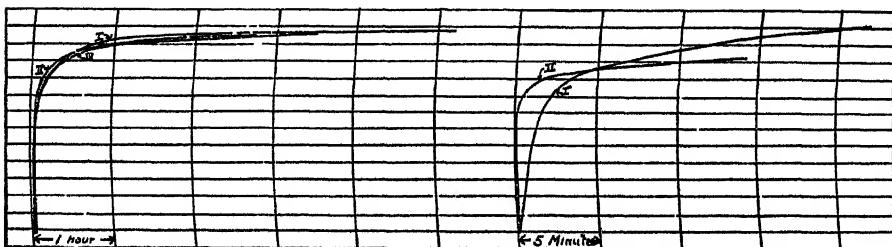


FIG. 3. CURVES OF THREE SOILS DEFLOCCULATED

- I. Webster silty clay loam
- II. Carrington loam
- III. Lintonia silt loam

FIG. 4. CURVES OF TWO SOILS DRAWN AS THOUGH RECORDING MECHANISM WERE REVOLVING TWELVE TIMES AS FAST

- I. Webster silty clay loam
- II. Carrington loam

rent carried up that through the torsion spring to the beam, all friction due to recording is eliminated from the beam.

The wiring diagram explains the electrical system of the recording mechanism. In order to obtain momentary electrical contacts for the sparks at regular intervals a mechanism of which a description has been published (2) was utilized. Switch *A* in the diagram was installed to give contacts other than the automatic ones whenever wanted. During the first five minutes

of the determination, the coarser particles settle so rapidly that more frequent contacts are necessary in order to secure the first part of the curve.

Figures 1-4 show curves obtained by the apparatus. These do not represent the entire soil, but only that portion consisting of very fine sand silt and clay from which the coarser particles have been sifted out. Seven-gram sam-

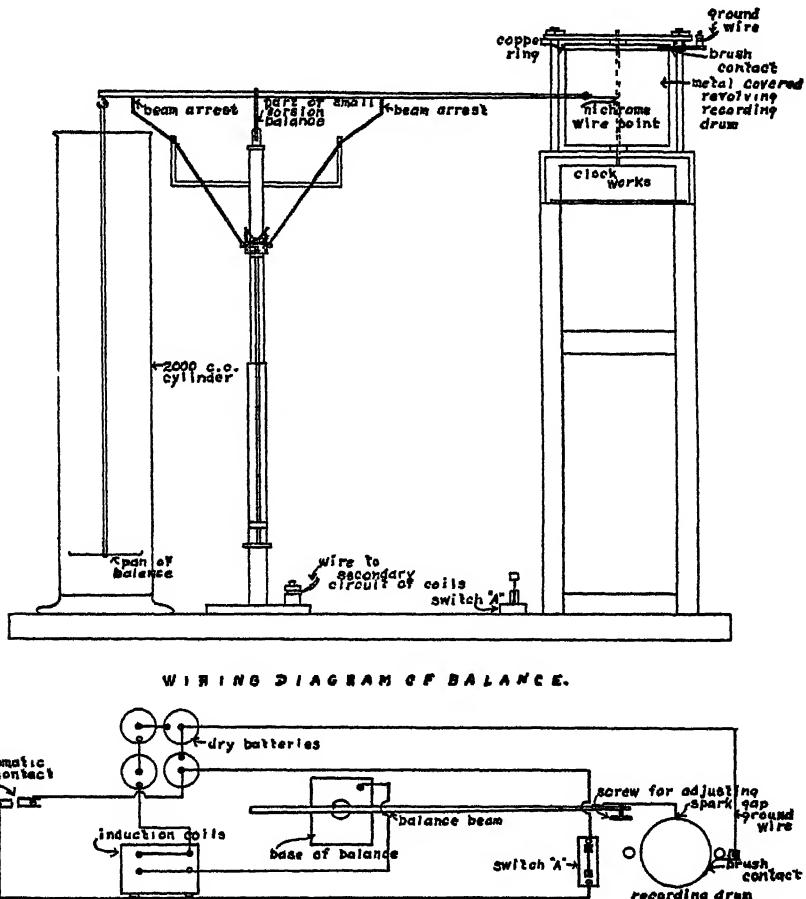


FIG. 5. AUTOMATIC RECORDING BALANCE ARRANGED FOR MAKING MECHANICAL ANALYSES OF SOILS

ples of the fine material were used. Since the balance pan was only two and one-half inches in diameter while the cylinder was three and one-fourth inches in diameter, only a little over four grams of soil would fall on the pan.

Figure 1 shows the points actually recorded by the apparatus. The points are not exactly on the line because of the fact that the spark does not always jump from the point perpendicularly to the cylinder. However the points

are sufficiently numerous to allow the drawing of curves as in this figure. Figures 2 and 3 give curves for three soils. In figure 2 the soils were shaken in distilled water for six hours and in figure 3, a few drops of ammonium hydrate were added to the distilled water and soil and solution shaken for six hours. The time of shaking was chosen arbitrarily because these were just trial runs. The recording drum made one revolution in twelve hours. In figure 4 the curves for two of the soils shown in figure 3 were reproduced by dividers so as to represent the recording cylinder as revolving twelve times as fast. In figures 2 and 3 all three soils appear similar but in figure 4 the differences are quite marked, because the chart is represented as having revolved twelve times as far during the intervals between sparks. If the recording cylinder made a revolution once an hour it is evident that the soil differences would be clearly shown.

In order to make a complete mechanical analysis a sulfur photometer could be used to determine the turbidity of the suspension after two hours settling. The clay content could be estimated by calibrating the photometer to indicate the amounts. A photometer has been used in some turbidity determinations here with good results.

This article is presented merely as a preliminary report that may lead others to further work along this line. It is hoped that the apparatus herein described may be perfected soon so as to be a very practical aid in soil investigations.

REFERENCES

- (1) ODEN, SVEN 1920 Die automatisch registrierende Sedimentiervorrichtung und ihre Anwendung auf einige kolloidchemische Probleme. *In Kolloid Ztschr.*, v. 26, p. 100-121.
- (2) JOHNSON, HARLAN W. 1923 An apparatus for making momentary electrical contacts at regular intervals. *In Jour. Indus. and Engin. Chem. (soon to appear).*

A COMPARISON OF SAND AND SOLUTION CULTURES WITH SOILS AS MEDIA FOR PLANT GROWTH

D. R. HOAGLAND AND J. C. MARTIN

University of California

Received for publication August 30, 1923

Several years ago, one of the writers (13) described certain experiments on the growth of barley plants in sand and solution cultures, and a number of general questions were raised pertaining to the interpretation of results obtained by the use of these methods. The experiments have been continued and it is now possible to extend the previous discussion. This appears to be the more desirable because of the wide application which is now being made of sand and solution cultures by plant physiologists and by investigators in agricultural experiment stations. It seems appropriate at the present time to inquire further into the possibilities and limitations of these methods. What factors are left uncontrolled in such experiments? What are the points of similarity or dissimilarity between solution, sand, and soil cultures? These and questions of like nature must be of interest to all who are concerned with the interrelations of plants and essential inorganic elements. It is our purpose in the present paper to invite a critical consideration of these questions and to offer some experimental data which seem to have a direct bearing on them.

Recently Davis (9) published an account of a comprehensive series of experiments carried on in this laboratory with wheat plants for the purpose of determining the influence of variability on the interpretation of data obtained from solution cultures. While the importance of the variability factor has long been recognized by biologists, its significance to plant-culture experimentation had been quite generally overlooked. The work of Davis makes it certain that small differences in dry weights of plants grown in solutions of slightly varying composition may have no meaning when the data are interpreted with regard to the probable error. In fact, at certain seasons of the year, Davis has found more recently (data not yet published) that the "best" and "poorest" solutions of the Shive series produced the same yields of wheat plants. These findings obviously point to the necessity for disregarding any differences of small magnitude in ordinary experimentation with a limited number of plants.

EFFECT OF DIFFERENT VOLUMES OF CULTURE SOLUTION ON PLANT GROWTH

In the previous article the writer emphasized (not, of course, for the first time) another factor which seems to have an important bearing on the interpretation of solution culture data. This is the change which takes place in the composition and concentration of a culture solution as a result of the absorption of ions by the plants. Under some circumstances, such changes

may be extremely rapid. Naturally the rate of change will depend upon the volume of solution provided for each plant, upon the concentration of the solution and upon the size and rate of growth of the plant. It should, therefore, be possible to obtain different results with the same solution simply by varying the size of the containers and the number of plants grown in each container.

An experiment was carried out to illustrate this point. Barley plants were grown for six weeks under the following conditions:

1. Regular culture solution, one plant in two liters, solution changed twice each week.
2. Dilute culture solution, one plant in two liters, solution changed three times each week.
3. Dilute culture solution, six plants in one liter, solution changed twice each week.

This simple experiment showed very clearly (table 1) that the same dilute solution may produce plants of very different sizes, depending upon the size of the containers and the number of plants grown in each container. By analyses of the residual solutions, it was shown that with treatment 1 the concentrations of the various ions were maintained at an approximately constant value throughout the growth cycle, whereas with treatment 3, plants several weeks old removed practically all of the potassium, nitrate, and phosphate before the end of three days. It was quite evident, therefore, that the actual cultural conditions were very different in these two cases, even though the same solution was used.

Not only was the yield of total dry matter altered, but also the composition of the plants as shown in table 1. The plants having at their disposal the larger volumes of solution contained a higher percentage of most of the elements of the culture solution.

The total concentration of the dilute solution was quite low, but similar considerations would apply to solutions of higher total concentration if the partial concentration of some rapidly absorbed ion were low, which condition would obtain in certain solutions of a series varying progressively in composition. The relative effects of different volumes of solution will depend upon the stage of growth of the plant and upon climatic conditions. A volume of solution which would be adequate for the growth of a plant in winter might become entirely inadequate in summer.

While it may be thought that these contentions require no argument, it is a fact that in many experiments which have been reported in recent years, insufficient attention has been paid to the rate of absorption of essential ions and to the total supply of these provided for each plant. Very recently, Trelease and Livingston (22) described an apparatus for growing plants in a continuously flowing solution, so that the roots may be bathed at all times in a solution of constant composition. Further comments on this procedure in relation to the soil solution will be made later.

TABLE I
Composition and yield of barley plants grown in different volumes and concentrations of culture solutions

CULTURAL CONDITIONS PERIOD OF GROWTH—JUNE 6-JULY 23				STEMS AND LEAVES				ROOTS				STEMS AND LEAVES				ROOTS			
				Composition				Composition				Total amount absorbed by each plant				Total amount absorbed by each plant			
				Average air-dry weight of each plant gm.	Average air-dry weight of each plant gm.	N	P	N	P	K	N	P	K	N	P	K	N	P	K
				per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	per cent	
1. 1 plant per 2 liters of solution of 1400 p.p.m. concentration. Total, 20 plants. Solution changed twice.	4.70	4.98	0.73	6.63	1.20	3.55	1.09	4.73	0.23	0.33	0.31	0.04	0.13	0.57					
2. 1 plant per 2 liters of solution of 200 p.p.m. concentration. Total, 20 plants. Solution changed three times a week..	3.33	4.59	0.64	4.88	0.74	2.55	0.60	3.98	0.15	0.02	0.16	0.02	0.004	0.30					
3. 6 plants per 1 liter of solution of 200 p.p.m. concentration. Total, 72 plants. Solution changed two times a week	0.91	2.98	0.92	3.50	0.32	1.96	0.49	2.10	0.03	0.008	0.03	0.006	0.002	0.07					

One other suggestion may be advanced on the basis of the data given in table 1. The solution of low concentration evidently was not quite so favorable to growth as the regular culture solution, even when the total volumes of solution provided were sufficient to maintain a practically constant composition. In other words, the concentration of certain ions may become so low that the plant cannot absorb them at a rate sufficiently rapid to permit maximum growth. Here also the climatic conditions must be taken into consideration. It should be noted, however, that very good growth may be obtained even with a solution of a total concentration as low as 200 parts per million. The relation of the concentration of phosphate to plant growth is especially interesting and several experiments bearing on this point will be presented later in this article.

AVAILABILITY OF IRON AND PLANT GROWTH

In addition to variability and the absorption of ions by the plant, the question of an adequate supply of iron in solution cultures has been neglected in many investigations. Gile and Carrero (11) early called attention to the importance of maintaining a suitable concentration of iron in the culture solution, and the subsequent work of one of the writers emphasized this point. It is now generally recognized (21) that the assumption that colloidal iron phosphate would supply to the plant a sufficient quantity of this essential element is by no means justified for all types of solutions. Under many conditions it is necessary to use other forms of iron, such as iron citrate or tartrate.

COMPARISON OF THE GROWTH OF PLANTS IN SOLUTION CULTURES AND IN SOILS

We can readily admit that the relation of plant growth to the composition of the culture solution constitutes a problem which justifies itself without reference to the soil. On the other hand, the investigator in this field naturally possesses an interest in the growth of plants in solid media, the normal condition for most plants of agricultural interest. Moreover, many solution culture investigations are undertaken by agricultural experiment stations with the avowed purpose of elucidating the nature of soil and plant interrelations.

During the past ten years, various members of the staff of this laboratory have been engaged on a study of a group of soils kept under controlled conditions, with particular reference to the composition of the soil solution as affected by season or by crop growth. We have, therefore, had a rather unique opportunity for making certain comparisons between soil conditions and solution culture conditions.

In our first series of experiments along this line, we grew barley plants in solution cultures adjacent to tanks of different soils which were under investigation. Three different solutions in 4-liter bottles were used. Only one

plant was placed in each bottle and no changes of solution were made. Small amounts of iron tartrate were added about once each week. The bottles were buried up to their necks in soil in order to maintain an even temperature around the roots. In addition to these cultures, another set was arranged, using 1-liter bottles (1 plant to each bottle) and changing solutions each week throughout the season. At several periods, small aliquots were removed from the bottles of each of the three first sets and the composite samples so obtained were analyzed. Observations on height, number of tillers, and stage of development of the plants grown in the artificial culture solutions and in the soil were made at frequent intervals and compared. After harvesting, the plants were separated into grain, stems and leaves, and roots.

Tables 2 and 3 show that after nine weeks, only very small concentrations of nitrate remained, especially in solutions *B* and *C*, which had lower initial concentrations of this ion. Potassium and phosphate were greatly diminished in concentration, while the diminution in the concentration of calcium, magnesium and sulfate was far smaller. In solution *C*, which was one-third as concentrated as solution *A*, the nitrate was reduced to a low level by the sixth week of growth. All the solutions were distinctly acid at the beginning but by the time that the plants had grown for six weeks the reactions had all changed to pH 6.8. This reaction was maintained during the remainder of the season.

Table 4 shows that the highest yield was obtained from the cultures in which the solutions were changed throughout the season. The yield of plants grown in the solution of low concentration was much smaller than in the other cases. For purposes of comparison, there is included in the table data on plants grown in a fine sandy loam soil, producing at the rate of 64 bushels of grain per acre. As already stated, the soil and solution cultures were located adjacent to each other and the plants started to germinate at the same date.

It is apparent that solutions *A* and *B* produced much larger plants than those produced by a fertile soil. One reason for this may be inferred from a study of Tables 2 and 3. At the end of six weeks, there remained in the artificial culture solutions a considerably greater concentration of nitrate than in the soil solution. During the first five weeks, the growth of the plants in the soil cultures and in the solution cultures was almost parallel, but beginning with the sixth week the plants in the solution cultures began to put out many more tillers than the plants in the soil and at the end of the growth period, the former plants had several times as many tillers as the latter. In the case of the dilute solution *C*, the growth of the plants during the first few weeks was practically equal to that in the other solutions, but the supply of nitrate was exhausted early and, although the plants started to produce a great many tillers, the concentration of nitrate was not maintained long enough to permit of the normal development of these tillers.

TABLE 2
Effect of the growth of barley plants on the composition of different culture solutions

PERIOD	K*			Ca*			Mg*			NO ₃ *			PO ₄ *			SO ₄ *		
	Solu-	Solu-	Solu-	Solu-	Solu-													
	tion A	tion B	tion C	tion A	tion B	tion C	tion A	tion B	tion C	tion A	tion B	tion C	tion A	tion B	tion C	tion A	tion B	
	<i>milli-equivalents</i>			<i>milli-equivalents</i>			<i>milli-equivalents</i>			<i>milli-equivalents</i>			<i>milli-equivalents</i>			<i>milli-equivalents</i>		
Initial.....	4.1	4.9	1.3	8.7	4.2	2.9	4.0	6.0	1.4	11.1	8.6	3.7	1.2	1.2	0.4	4.5	6.3	1.5
After 6 weeks' growth.....	2.0	3.6	0.4	7.5	3.6	2.4	†	†	†	5.7	4.0	0.6	0.8	0.9	0.2	3.9	5.8	1.1
After 9 weeks' growth.....	0.4	1.4	0.1	5.9	2.9	1.9	3.1	4.7	1.1	2.6	0.2	0.1	0.2	0.3	0.03	3.0	4.8	0.9
At time of harvest, 17 weeks.....	0.4	0.9	0.2	2.6	1.6	0.9	1.0	2.1	0.2	0.0	0.0	0.0	0.2	0.2	0.04	†	†	†

* In addition to the elements listed above, there was added to these solutions approximately 0.5 p.p.m. Mn as the sulfate. Iron was added at intervals in the form of ferric tartrate. The solutions also contained small amounts of sodium chloride, from 5 to 25 p.p.m.

† Determinations lost.

‡ Some evidence of bacterial decomposition, determinations not made.

TABLE 3

*Change of concentration of NO_3^- in soil solution during growth of barley crop**

PERIOD	CONCENTRATION OF NO_3^-
At planting date.....	milli-equivalents
After 2 weeks.....	3.7
After 4 weeks.....	7.4
After 6 weeks.....	6.1
After 8 weeks.....	1.6
After 10 weeks.....	0
After 12 weeks.....	0
After 14 weeks.....	0

* These data were obtained on a tank of fine sandy loam soil (No. 11), located adjacent to the solution culture experiments.

TABLE 4

Description of barley plants grown in solution and soil cultures

CULTURES	TOTAL NUMBER OF PLANTS	AVERAGE HEIGHT OF PLANTS cm.	AVERAGE NUMBER OF HEADS PER PLANT	AVERAGE WEIGHT OF HEADS PER PLANT [§] gm.	AVERAGE NUMBER OF TILLERS	AVERAGE WEIGHT OF STALK PER PLANT [§] gm.	AVERAGE WEIGHT OF GRAIN PER PLANT [§] gm.	AVERAGE WEIGHT OF KERNELED GRAIN PER PLANT [§] gm.	TOTAL DRY MATTER IN GRAIN per cent
Solution A.....	19	100±1.8†	21±0.62	24±1.5	25±0.77	36±1.7	22	0.043	37
Solution B.....	20	106±1.6	15±0.48	20±1.1	17±0.51	28±0.80	16	0.047	33
Solution C.....	16	73±1.6	10±0.29	7±0.42	14±0.41	14±0.31	5	0.038	24
Solution A (frequent changes)	15	95±2.6	32±0.99	55±1.6	41±1.3	54	48	0.041	44
Soil*.....	35†	104±1.5	7±0.36	12±0.70	8±0.34	10±0.47	10	0.049	45

* The crop grown on this soil (No. 11), yielded at the rate of 64 bushels of grain per acre.

† Area of soil allowed for growth of each plant 36 sq. in.

‡ Probable error of the mean.

§ On air-dry basis.

Details of experiment

Solutions, A, B and C remained unchanged during the entire season, but 4-liter bottles were used and only one plant was placed in each bottle. These bottles were buried in the ground up to their necks.

For solution A (changed frequently), 1-liter bottles with one plant in each bottle were used. In this case, the solutions were changed at approximately weekly intervals throughout the season.

Period of growth, May 13 to October 1.

Solution A had an entirely different composition from solution B. In solution A the equivalent weight of calcium was more than twice that of magnesium, while in solution B more magnesium was present than calcium. Solution A, it is true, produced a slightly greater yield of dry matter than

solution *B*, but if this difference is significant it can be attributed to the difference in the concentration of nitrate in the two solutions. There is no reason to believe that the different ratios between the various ions had any effect on growth. In the experiments of Davis already mentioned, it was found that solutions of widely different composition produced equal weights of wheat plants within the experimental error.

The plants grown in the changed solutions were of exceptional size. They continued to put out new tillers for a much longer period than the other plants. The increased growth was not merely vegetative, however, since the total grain produced by each plant was also much greater. In fact the proportion of grain to total dry matter exceeded that for the other plants. The ripening processes were, however, much delayed.

Some striking differences in composition are recorded in table 4. The plants grown in the frequently changed solution had an entirely different composition from that of the plants grown in a similar solution unchanged. In the changed solution the percentage of nitrogen and potassium in the straw was much higher. In the grain, the percentages of calcium, magnesium and potassium were all very much the same but the nitrogen content of the grain from the plants grown in the frequently changed solution was much higher than that from the plants grown in the unchanged solution. The percentage of phosphorus was also significantly increased. The difference in the composition of solutions *A* and *B* was reflected in the composition of the straw and of the roots. This difference was especially noticeable for the percentage of calcium in the straw. There was an entirely different ratio of calcium to magnesium in the two cases, but as we have indicated already, this fact probably has no significance in so far as the total yield of crop is concerned.

COMPARISONS OF THE GROWTH OF PLANTS IN SAND AND SOLUTION CULTURES

A very important consideration should be kept in mind in planning experiments with sand cultures. If these are to be compared with solution cultures, the same volume of solution should be provided for each plant in both cases. This obviously means that much larger containers must be provided for the sand cultures than for the solution cultures. For example, if one liter of solution is provided for a given number of plants in a solution culture, then there would be required for a comparable sand culture (at 12.5 per cent moisture content) eight kilograms of moist sand. Unfortunately in almost all of the sand culture experiments heretofore reported, this precaution has been neglected and the amounts of sand used have been so small that the total amounts of culture solution available to the plants have been very restricted. Under these circumstances, it may well have happened that the growth of the plants was limited by an inadequate supply of one or more essential elements. There is considerable inconvenience attendant upon the use of large jars and large quantities of sand, but it is essential, nevertheless, to

give heed to the volumes of culture solution provided. Disregard of this matter may also lead to erroneous ideas concerning the effect of different hydrogen-ion concentrations on plant growth, since the initial reaction of the solution may be changed with extreme rapidity.

Barley was grown in both sand and solution cultures. One liter of solution was provided for each plant and six changes of solution were made during the experiment. The plants were twelve weeks old when harvested. The method of McCall (17) was used in making the changes on the sand cultures. The seeds were planted in the sand cultures at the same time that the seeds for the solution cultures were placed in the germinating pan, both at the same temperature. If seeds already germinated are afterward transplanted to sand, the roots are likely to be injured and a temporary inhibition of growth may take place.

TABLE 5

Composition of barley plants (at maturity) grown in different solutions

CULTURES	K			Ca			Mg			N			P		
	Straw	Grain	Roots												
	per cent														
Solution A.....	1.19	0.50	0.57	1.05	0.10	0.56	0.29	0.15	0.12	0.41	1.29	0.69	0.14	0.39	0.26
Solution B.....	1.78	0.50	1.05	0.58	0.06	0.33	0.32	0.16	0.20	0.36	1.26	0.65	0.15	0.45	0.24
Solution C.....	0.75	0.48	0.95	0.96	0.07	0.32	0.26	0.17	0.15	0.45	1.36	0.49	0.15	0.50	0.21
Solution A*....	2.72	0.52	0.59	1.17	0.08	0.40	0.33	0.16	0.34	0.92	2.14	1.39	0.15	0.54	2.63
Soil†.....	1.80	0.51		0.54	0.05		0.21	0.13		0.34	1.41		0.08	0.44	

* Changed frequently.

† Fine sandy loam soil yielding at rate of 104 bushels of grain per acre. (Not the same soil as that referred to in table 3). Area of soil allowed for growth of each plant 18 sq. in.

Although the number of plants employed in this experiment were too few in number, the differences in the composition of the plants grown under the two different conditions are significant (table 6). Except for phosphorus in the stems and leaves, larger percentages of all the elements were found in the plants grown in the solution cultures. A larger dry weight of plants was obtained, however, from the sand cultures.

In another experiment (table 7), the plants were grown to maturity. Each plant was provided with 1500 cc. of solution and no changes of solution were made. Here again the percentages of inorganic elements were higher in the plants grown in the solution cultures. Also, the yield from the sand cultures was greater than that from the solution cultures, especially the yield of grain. The percentage of grain and the average weight of kernels were greater in the case of the sand cultures.

In these and in other experiments we have noted that tillering proceeds more rapidly in sand cultures than in solution cultures. This fact may, perhaps, be explained on the basis of the more profuse development of root sys-

TABLE 6
Composition of plants grown in sand and solution cultures

CULTURE	AVERAGE AIR-DRY WEIGHT OF EACH PLANT	STEMS AND LEAVES					ROOTS				
		K	Mg	Ca	N	P	K	Mg	Ca	N	P
		gm.	per cent				gm.	per cent			
Sand—12 plants.....	26.3	2.43	0.35	0.90	2.25	0.64	0.97	0.26	1.04	1.36	0.35
Solution—12 plants.....	13.8	3.25	0.49	1.48	2.98	0.61	1.60	0.34	2.62	2.66	1.32

Details of experiment

The plants were grown from July 23 to October 20.

One liter of solution was used for each plant. 6 changes of solution for both solution and sand cultures. The same total quantities of solution were provided for each plant in both solution and sand cultures.

TABLE 7
*Comparison of yields and of composition of barley plants grown in sand and solution cultures to maturity**

	AVERAGE WEIGHT (WATER- FREE BASIS) OF EACH PLANT	COMPOSITION				
		K	Ca	Mg	N	P
	gm.	per cent	per cent	per cent	per cent	per cent
<i>Sand culture:</i>						
Stems and leaves.....	6.63	1.52	0.89	0.32	0.44	0.09
Chaff.....	1.50	1.31	0.61	0.35	0.50	0.13
Grain.....	9.92†	0.47	0.06	0.12	1.54	0.38
Entire plant (roots excluded).....	18.05					
<i>Solution culture:</i>						
Stems and leaves.....	6.17	2.21	1.40	0.43	0.77	0.24
Chaff.....	1.67	1.70	0.82	0.31	1.00	0.32
Grain.....	6.00‡	0.63	0.06	0.14	1.89	0.51
Entire plant (roots excluded).....	13.54					

Description of plant (grown from May to September)

CULTURE	NUMBER OF PLANTS GROWN	AVERAGE HEIGHT cm.	AVERAGE NUMBER OF HEADS PER PLANT	AVERAGE AIR-DRY WEIGHT OF HEADS PER PLANT gm.	AVERAGE NUMBER OF TILLERS PER PLANT	AVERAGE AIR-DRY WEIGHT OF STRAW PER PLANT gm.	AVERAGE AIR-DRY WEIGHT OF KERNELS gm.
Sand.....	24	74.7±0.82§	12.0±0.55	12.3±0.42	12.7±0.57	7.13±0.26	0.050
Solution.....	24	74.8±0.92	11.5±0.38	8.1±0.31	12.0±0.33	6.50±0.33	0.039

* Total volume of culture solution supplied to each plant was 1500 cc., the same in both solution and sand cultures.

† 55 per cent of entire plant.

‡ 43 per cent of entire plant.

§ Probable error of the mean.

tems in sand cultures. Gericke (10) has suggested that tillering is related to root development. If it is a fact that a sand culture offers a more favorable medium for plant growth than a solution culture, the explanation cannot be based on the total intake of essential elements, since plants developed under solution culture conditions may have the higher percentage of these elements. There are other differences in the conditions of sand and solution cultures. Very appreciable amounts of silica derived from the sand enter into solution and plants grown in sand may contain considerable quantities of silica in the stems and leaves. The conditions of aeration are, of course, different in these two types of cultures, and this is sometimes considered the principal difference.

THE SOIL SOLUTION IN ITS PHYSIOLOGICAL ASPECT

The ideas which are now held concerning the soil solution as a medium for supplying essential elements to plants have been reviewed by Burd and Martin (5).

The original investigations of this laboratory on the soil solution began with a study of water extracts of various soils kept in tanks under conditions as carefully controlled as possible. It was found in general that these water extracts were subject to great changes in composition and concentration during the course of the year. The growth of barley and of other plants had a pronounced influence in diminishing the quantity of material which could be extracted with water. The most notable change was in nitrate, which was generally reduced to a negligible concentration by the time the plants had made their maximum growth. Definite decreases in the amounts of water extractable calcium and magnesium also occurred at this time. The decreases in potassium were less marked in character but they seemed to be significant in the majority of soils examined. No clear evidence was obtained of consistent changes in water extractable phosphate during a single season.

At the time that the investigations were begun, the methods of water extraction seemed to be best adapted to achieve the purposes in view. It was realized, however, that an extract made with five parts of water to one of soil, was not identical with the soil solution. Shortly afterward, Bouyoucos and McCool (2) described a cryoscopic method for determining the concentration of the soil solution at any desired moisture content. This method (12) was applied to the same soils which were being studied by means of water extracts. There was found to be a good general agreement between these two methods as far as general changes in total concentration were concerned. Both procedures indicated that the concentration of solutes in the soil moisture varied at different times during the season and that there was a significant decrease in concentration brought about by the growth of crops.

Measurements of the freezing point depressions of the soil solution *in situ* were supplemented by observations on extracts of several soils (15) made with very small proportions of water, after these extracts had been concentrated so as to have the same depressions as those of the corresponding soils at approximately the optimum moisture content. It was found that these concentrated extracts could be passed through another portion of the moist soil without essential change, and it was thought that this evidence justified the conclusion that a solution possessing such properties did not differ greatly from the actual soil solution, as it existed in the soil under those particular conditions.

The results of these various lines of inquiry led to the assumption that water extracts, while not themselves identical with the soil solution, did reflect changes in this solution in a consistent manner. At this stage of the investigations the only direct evidence concerning the total concentration of the soil solution was that based on freezing point depressions. An attempt was made to use these data for the purpose of computing the quantity of material dissolved from the soil by a 1-5 extract, in addition to such material contained originally in the soil solution. Before performing such computations, it was essential to decide whether

or not all of the soil moisture was effective as a solvent. If it were assumed that all of the soil moisture acted as a solvent, then the amount of additional material dissolved by the 1-5 extract could not be considered very great in most cases. But Bouyoucos found that when the freezing point depressions of soils were determined at different moisture contents, there was an abnormally great increase in the values obtained under low moisture conditions. This observation led to the theory that a considerable proportion of the total moisture of a soil might be held in "unfree" form and not act as a solvent. The amount of unfree water would vary greatly with different soils. On this basis, the total amount of dissolved material contained in a given mass of soil would be less than if all of the water functioned as a solvent. On the basis of the unfree water hypothesis, it was estimated that the 1-5 water extracts dissolved from the soils used in our investigations a considerable quantity of material not originally present in the soil solution.

Later Keen (16) made a mathematical analysis of some of the freezing point data published by Bouyoucos and showed that there was no sharp line of demarcation between the different forms of water in the soil and also suggested that the proportion of unfree water was not constant, but varied with the total moisture content. These conclusions are not accepted by Bouyoucos (1), who states that dilatometer measurements indicated that the unfree water was sensibly constant regardless of the total water content of the soil.

About this time Parker (19) published a description of a modern application of what may be regarded as one of the oldest methods for studying the soil solution, the displacement method. As an incident to this investigation, Parker reached the conclusion that depressions of the freezing point may not measure the true concentration of soil solutions, since the finely divided or colloidal material of the soil exerts a pronounced effect on the freezing point depression, regardless of the solutes contained in the soil solution. Parker further concluded that all or nearly all of the water in soils functions as a solvent.

The question of whether finely divided material in itself produces a lowering of the freezing point as suggested by Parker, is an interesting one and the writers have made some measurements on aluminum oxide (Baker's analyzed, 200-mesh fine) at different moisture contents. When the oxide was washed free from soluble impurities, it was found that there was no appreciable depression of the freezing point, even at the lowest moisture contents at which a determination could be made. Sugar solutions added to the dry aluminum oxide had practically the same freezing point depression as in the free state.

While it is therefore not proved that merely finely divided material affects the freezing point depression, yet it is a fact that the solution displaced from a soil at a low moisture content may be much less concentrated than would be inferred from the freezing point depression made on the soil at the same moisture content. But so far it does not appear that freezing point depressions made on soils (at least on those used in our experiments) at optimum moisture content are affected to more than a slight extent by these new considerations. We have frequently found that soils at the time of the most active absorption of solutes by a barley crop showed extremely small depressions of the freezing point, yet the influence of the finely divided or colloidal material must have been exerted at all times during the season. Also, Burd and Martin (5) have found only comparatively slight differences between the freezing point depressions of soils and those of the displaced solutions, when moisture contents were not below the optimum.

Recently Burd and Martin (5) made an extensive and critical study of the Parker displacement method and introduced several modifications in the technique. The results of their experiments have a very significant bearing on the questions now under discussion. The simplest interpretation of the data would exclude the idea that any important amount of water in the soil does not act as a solvent. If this conclusion be correct, then it is unnecessary to take into account unfree water in comparing the amounts of material present in a water extract and in the soil solution. In other words, the water extract is made up more largely of solutes derived from the soil solution than was at first assumed. Nevertheless, Burd and Martin have shown that 1-5 extracts of the soils examined by them contained

larger amounts of certain solutes, particularly of potassium and phosphate, than were found in the soil solution. All considerations lead to the same conclusion with regard to phosphate, namely, that this ion is likely to exist in the soil solution only in very low concentration, and that the excess of phosphate dissolved in a water extract is very great.

Some of these conclusions were confirmed by still another method. Burgess (7) working in this laboratory, applied the Lipman pressure method to the study of a group of fine sandy loam soils and from his studies reached the conclusion that unfree water did not exist to any appreciable degree in these soils.

It is beside the purpose of the present discussion to consider the forms of water in a soil, but it may be remarked in passing that it seems possible that water may sometimes be combined or adsorbed and yet act as a solvent. Browne (4) suggests that a similar condition exists in ferric oxide hydrosols. We must acknowledge, however, that these questions cannot be regarded as settled at the present time.

CONCENTRATION OF PHOSPHATE IN SOIL SOLUTIONS AND IN CULTURE SOLUTIONS

One of the most striking differences between a soil solution and an artificial culture solution is found in the concentration of phosphate. Even a fertile soil may contain only a very low concentration of phosphate in its solution. Burd and Martin demonstrated this point by means of the displacement method. The series of fine sandy loam soils examined by them contained 3 to 12 parts per million of the phosphate ion in the solutions obtained from the uncropped soils. In ordinary culture solutions, the initial concentration of phosphate is far higher than this. For example, in one of Shive's solutions, approximately 1400 parts per million of this ion are present. Can plants be grown in culture solutions with concentrations of phosphate similar to those found in soil solutions? Comber (8) has suggested that plants may absorb phosphate from soils in a different way than they do from artificial culture solutions.

The authors, accordingly, carried out experiments (tables 8, 9, and 10) during two seasons for the purpose of studying the growth of plants in culture solutions with very low concentrations of phosphate. These experiments were attended with some difficulty since it was necessary to maintain the concentrations of phosphate fairly constant. The procedure adopted was to use large volumes of solution and to add at frequent intervals new portions of phosphate, in the form of KH_2PO_4 . After the plants had grown for several weeks it was necessary to make these additions every day. In order to control the concentrations, small samples of solution were removed from each bottle several times each week, and these samples composited for analysis. Very good growth of barley plants occurred in solutions with concentrations of phosphate as low as those of the soil solution. In the first season's experiment, the supply of essential elements other than phosphate was very abundant and the yield obtained from the solution with an average of 9 parts per million of phosphate was greater than those from the solutions containing 0.7 or 2.4 parts per million. But even with the lowest concentration of phos-

phate, the average dry weight of each plant was greater than that of plants grown at the same season in soils producing at the rate of 25 to 65 bushels of grain per acre. In the second experiment, the concentration of the culture solution was reduced to one-third of that employed during the first season, and the solution of 10.8 parts per million of phosphate did not produce any greater yield than that containing 3 parts per million of phosphate. The

TABLE 8

Comparison of yields and composition of barley plants grown in solutions of different concentrations of PO_4

	AVERAGE WEIGHT (WATER- FREE BASIS) OF EACH PLANT gm.	COMPOSITION				
		K percent	Ca percent	Mg percent	N percent	P percent
<i>Solution of 0.7 p.p.m. PO_4:</i>						
Stems and leaves.....	6.13	3.48	1.77	0.34	1.85	0.32
Chaff.....	1.70	2.00	1.04	0.34	1.84	0.52
Grain.....	4.60	0.77	0.08	0.16	2.58	0.59
Entire plant (roots excluded).....	12.43					
<i>Solution of 2.4 p.p.m. PO_4:</i>						
Stems and leaves.....	9.50	3.44	1.74	0.42	1.69	0.27
Chaff.....	2.80	1.76	0.91	0.36	1.66	0.42
Grain.....	5.40	0.59	0.10	0.16	2.84	0.63
Entire plant (roots excluded).....	17.70					
<i>Solution of 9.0 p.p.m. PO_4:</i>						
Stems and leaves.....	10.80	2.90	1.48	0.48	1.05	0.23
Chaff.....	2.97	1.99	0.86	0.36	1.17	0.33
Grain.....	9.60	0.74	0.08	0.15	2.32	0.58
Entire plant (roots excluded).....	23.37					
<i>Regular culture solution, 120 p.p.m. PO_4:</i>						
Stems and leaves.....	6.17	2.21	1.40	0.43	0.77	0.24
Chaff.....	1.67	1.70	0.82	0.31	1.00	0.32
Grain.....	6.00	0.63	0.06	0.14	1.89	0.51
Entire plant (roots excluded).....	13.84					

solution containing 1.1 parts per million yielded almost as much in total dry matter as either of the others. All the solution cultures produced larger plants than those produced by a soil yielding at the rate of 40 bushels of grain per acre. In the soil cultures, the plants were spaced more widely than in ordinary field practice. Further reference to this latter point will be made presently.

TABLE 9
Description of barley plants grown in solutions of different phosphate concentration
(Air-dry basis)

DESCRIPTION OF SOLUTION	TOTAL NUMBER OF PLANTS	AVERAGE HEIGHT	AVERAGE NUMBER OF HEADS PER PLANT	AVERAGE WEIGHT OF HEADS PER PLANT	AVERAGE NUMBER OF TILLERS PER PLANT	AVERAGE WEIGHT OF STRAW PER PLANT	AVERAGE WEIGHT OF AIR-DRY GRAIN PER PLANT	PROPORTION OF GRAIN IN TOTAL DRY MATTER	
								gm.	per cent
0.7 p.p.m. PO_4	30	70.3±0.59*	13.9±0.53	6.95±0.40	16.2±0.61	6.76±0.31	4.60	0.033	40
2.4 p.p.m. PO_4	30	77.0±0.88	19.7±0.75	9.28±0.30	21.4±0.75	10.95±0.35	5.40	0.033	33
9.0 p.p.m. PO_4	30	78.5±0.87	21.3±0.84	14.22±0.64	22.4±0.85	12.68±0.51	9.60	0.034	43
Regular solution, 120 p.p.m. PO_4	24	74.8±0.92	11.5±0.38	8.08±0.31	12.0±0.33	6.50±0.33	6.00	0.039	48

* Probable error of the mean.

Details of experiment

The concentration of phosphate in the first three solutions was maintained approximately as indicated above by the daily addition of small amounts of KH_2PO_4 . Samples of the solutions were taken every few days and analyzed for PO_4 . Four-liter bottles were used with 2 plants in each bottle. The solution was changed once after 39 days of growth. Plants in regular culture solution were grown in 2-liter bottles with 2 plants in each bottle and here the solution was not changed.

The average weight of grain for individual plants from adjacent soil cultures was 3.0 gm. This is an average of 13 soils yielding at the rate of 25 to 65 bushels per acre.

The average weight of the total dry matter per plants was 6.0 gm.

The number of plants grown in the tanks of soil allowed a space of 17 sq. in. for each plant.

TABLE 10

Description of barley plants grown in solution of different phosphate concentrations

DESCRIPTION OF SOLUTION	TOTAL NUMBER OF PLANTS	AVERAGE HEIGHT	AVERAGE NUMBER OF HEADS PER PLANT	AVERAGE WEIGHT OF HEADS PER PLANT	AVERAGE NUMBER OF TILLERS PER PLANT	AVERAGE WEIGHT OF STRAW PER PLANT	AVERAGE WEIGHT OF GRAIN PER PLANT	AVERAGE WEIGHT OF KER- NELS	PROPORTION OF GRAIN IN TOTAL DRY MATTER per cent
		cm.	gm.	gm.	gm.	gm.	gm.	gm.	
1.1 p.p.m. PO ₄ ..	30	79±0.76*	5.0±0.13	5.6±0.21	5.4±0.04	3.4±0.04	4.6	0.036	50
3.0 p.p.m. PO ₄ ..	30	80±1.0	4.8±0.16	5.1±0.23	5.4±0.15	4.6±0.17	4.2	0.034	43
10.8 p.p.m. PO ₄ ..	30	83±0.82	4.3±0.04	5.0±0.21	5.0±0.17	4.8±0.16	4.2	0.039	43

* Probable error of the mean.

Details of experiment

Four liters of solution in each bottle supported two plants. The solution had one-third the concentration of that used in preceding experiment and was not changed.

The average amount of grain produced by a plant on adjacent soil was 3 gm. This soil yielded 40 bushels per acre.

Average total dry matter per plant was 6.3 gm.

GENERAL COMPARISONS BETWEEN PLANTS GROWN IN SAND, SOIL AND SOLUTION CULTURES

While in recent years, many experiments have been reported in which the technique of solution or of sand cultures has been used, ordinarily no detailed description of the plants is given. Some of the photographs published show plants that seem to be more or less stunted even though grown in what were considered the best solutions. That is to say, even though the composition of the culture solutions was entirely favorable, some other condition may have limited growth. At certain seasons climatic factors may have been responsible but in other cases it is extremely probable that the total volume of solution supplied to each plant was inadequate.

What constitutes a normal plant and upon what basis should comparisons be made between plants grown under different conditions? Under a favorable climatic environment, it is possible to produce from a single barley seed a plant with as many as forty tillers and thirty or more heads. Individual plants from fertile soils under ordinary conditions of planting are much smaller than this. The size of the individual plants produced in a soil depend in part upon the number of plants grown in a given area or volume of soil. Within rather wide limits, the total yield from a given mass of soil may be relatively constant regardless of the number of plants [Brenchley (3) and Burd in some unpublished data]. In much the same way, the size of the plant produced in solution or sand cultures will vary with the volume of solution, the number

of plants grown in each container, and the number of times the solution is changed. For this reason (cf. table 1), it is possible to obtain plants of entirely different size, the total growth depending upon the capacity of the container and the frequency with which the solution is changed. If the climatic conditions are not sufficiently favorable, a small amount of culture solution may be capable of producing plants as large as can be grown under that particular aerial environment. This will also be true if plants are grown only for short periods.

From this discussion it is apparent that normality as applied to plant growth is a relative term. We are not justified in saying that a normal plant is one making the best growth under a given set of environmental conditions since it is evident that certain environments would affect the plant adversely. Thus a certain plant would be the best that could be grown under certain particular conditions yet would be abnormal when compared to plants grown under more favorable environments. Normal plants may vary in total growth and may be produced under a relatively wide range of conditions. With these facts in mind it is evident that no exact standard for a normal plant can be established. It might be permissible to accept as a standard for comparison a plant of the same species grown in a productive soil and under similar climatic conditions.

If it is desired to make any exact comparisons of different solutions with reference to the growth of plants over extended periods, it is necessary either to use large volumes of solution for each plant or else to use a continuously flowing solution, as suggested by Trelease and Livingston (22). By this means, the composition of the culture solution may be maintained constant and very interesting information obtained in connection with certain problems, but the comparison of many different solutions in this way would involve great technical difficulties.

In view of some unpublished findings by Davis and in consideration of what has already been said here, it is fair to question the profit in comparing solutions of slightly varying composition. At least, more should be required than the control of the culture solutions. The adequacy or the toxicity of any given solution or cultural arrangement is very much dependent upon climatic conditions. This fact is strikingly illustrated by the recent experiments of Davis in which it was found that two solutions of extremely different composition produced equally good yields of wheat during certain months of the year and during other months produced significantly different yields. Not the least important factor of the climatic complex is light. One of the writers has found that even comparatively slight shading during the summer months decreased the growth of barley plants to a marked degree and altered their composition with regard to inorganic elements even though the temperature was maintained at essentially the same point around the shaded and the fully illuminated plants.

Our present knowledge enables us to state with considerable assurance that we cannot hope to demonstrate a "best" solution for any plant. It cannot be expected that any two investigators will agree in their findings unless all conditions, light, temperature, humidity, volumes of culture solution, variability, etc., are controlled. The relations of a plant to its culture medium are dynamic and no solution has any fixed value for plant growth. These remarks are made in a constructive spirit and are not directed in opposition to those who have initiated such researches in the field of plant nutrition.

There is still another phase of experimentation with plants in artificial cultures which has perhaps received insufficient attention. Most culture solutions are made up with only six elements, aside from iron. It is probable that other elements may be essential, at least in small amounts. McHargue (18) has demonstrated this to be so in the case of manganese. In our experiments with barley, we have not found manganese necessary, but this may only mean that sufficient manganese was present as an impurity in the salts used. In determining the essential nature of elements required, probably in traces only, it becomes necessary to employ highly purified salts. Even then, an ample supply may be furnished by the seed.

EXPRESSING THE COMPOSITION OF CULTURE SOLUTIONS

The triangular diagram system is ingeniously adapted to the presentation of the data on yields obtained from many different solutions, but in view of the difficulties met with in the interpretation of such data, it is possible that the diagrams sometimes may become misleading. It may also be suggested that it is desirable to place the emphasis on the ions of the solution rather than on the salts used in preparing them. It is admitted that in a complex culture solution, the chemist is not prepared to speak with any certainty concerning the concentrations or activities of individual ions. Nevertheless, the culture solutions are ordinarily very dilute and the degree of dissociation high. Also, as plants absorb ions from the solutions undissociated molecules dissociate to restore the equilibrium. There is much evidence from absorption studies that plants absorb the elements of the culture solution in ionic form (14).

In earlier work, we have been accustomed to express the composition of culture solutions in terms of parts per million. Undoubtedly this method served the purposes in view at that time but with the carrying out of more intensive studies it has become necessary to interpret the data in terms of chemical equivalents. It seems to the authors that the most satisfactory method of describing culture solutions in all experiments of the type now under consideration, is in terms of milliequivalents. (In water analysis, these are called reaction values.) Total concentrations may be expressed in terms of parts per million or as osmotic pressures even though osmotic pressure may not have any particular physiological significance in dilute culture solutions.

INTERPRETATION IN RELATION TO SOIL PROBLEMS

It may be well to consider further some of the similarities and dissimilarities between growth conditions in soil and solution cultures. One of the methods frequently employed with solution cultures is to change solutions every three days throughout the growth cycle of the plant. The plant is, therefore, subjected to alternating conditions in the culture medium. Conditions in the soil are likely to be quite different from this. The soil solution gradually decreases in concentration during the growth of the plant and during the latter stages very little nitrate remains in the soil solution. There may also occur a decrease in the concentration of calcium, magnesium, and potassium. Phosphate may possibly increase in concentration, because of the withdrawal of certain cations from the solution, as suggested by Burd and Martin (6). Later studies (unpublished data), indicate that during the growth of barley plants in soils which are not subject to leaching and in which the calcium concentration is only slightly decreased, the phosphate concentration is significantly lowered. A continuously flowing solution also fails to provide a medium like that of the soil, although this is no argument against the use of such technique for special purposes.

Probably the conditions in the experiment described on page 379 imitated soil solution conditions to a considerable extent. In this experiment, the solution was not changed and the concentration of ions was decreased by absorption by the plant. It is probable, however, that potassium was reduced to a lower concentration than in most soil solutions.

Aside from phosphate, the authors have found no fundamental dissimilarity in composition or concentration between culture solutions such as those described in table 2 and soil solutions displaced from soils early in the season. It does not seem to be necessary to assume that plants absorb essential elements from soils by some special mechanism entirely different from that operative in solution cultures.

While the composition of the solution displaced from a soil may represent, on the average, the solution from which plants absorb their mineral elements, there are undoubtedly certain complications introduced by the presence of the solid medium. The composition of the soil solution in immediate contact with absorbing roots may not be the same as that displaced from the mass of the soil as a whole. Diffusion of ions in soils is far slower than in solution cultures, and the absorption of ions from the soil solution seems to depend to a great extent upon the ability of the plant to extend its root system (20). It would seem that the nitrate ion diffuses readily through the soil solution since all, or practically all of the nitrate is removed from a soil contained in a tank even though the absorbing roots do not come into contact with every portion of the solution. Different ions diffuse at different rates and this fact would also have to be considered in drawing deductions regarding what may be called the "physiological selection." It is also probable that as root growth

and the absorption of ions proceed, not all of the root system would be bathed at any one time in exactly the same soil solution. In solution cultures, diffusion must be extremely rapid. Sand cultures would partake of the nature of the soil to a limited extent. The differences in the rates of diffusion of ions in sand cultures and in solution cultures is reflected in the composition of the plants grown in sand and solution cultures, as we have already pointed out. On the other hand, in both sand and soil cultures, the proportion of roots to tops is much greater than in solution cultures. The comparisons which have just been made refer particularly to soils kept at the optimum moisture content. Burd and Martin (5) have shown that as the moisture content of a soil decreases, the concentration of some of the ions of the soil solution increases almost proportionately, so that the effect of variations in the moisture content of the soil, often occurring during the season, must be taken into consideration. While the concentration of the soil solution is increased at low moisture contents, the physiological availability of ions and of water may be decreased and it is impossible at present to determine the nature of the physiological relations existing between the plant and the soil solution at low moisture contents.

Notwithstanding that solution culture conditions are in certain respects abnormal for most agricultural plants, plants like barley can be carried through their complete cycle of growth and very large and well developed plants can be produced. There is one difficulty which is often encountered at the final stage of growth under solution culture conditions. Roots may undergo bacterial decomposition at this time so that the final ripening of the grain is interfered with. In several experiments, however, we have found the average weight of the kernels produced in solution culture about 80 per cent of than the weight of those produced in a good soil. We have also compared the relative germinating powers of seeds grown under these different conditions and have found no differences.

GENERAL DISCUSSION

This survey of experiments leads to several general conclusions. As might naturally be expected, plants have great powers of adaptation to different cultural conditions. It is not at all necessary that some specific solution be provided. The essential condition of good growth, as far as the mineral elements are concerned, is that the concentration of each element be maintained above its critical level. The culture solution must be replenished as absorption of ions by the plant proceeds in order to maintain the concentration of any essential element above its critical concentration. Finally the conditions of light and temperature are of paramount importance in determining the adequacy of concentration of any essential element.

Although it has been the purpose of this article to point out some of the many difficulties to be overcome in interpreting, in terms of soil problems,

data obtained from experiments with artificial culture solutions, it is not intended to depreciate the value of such experiments. Indeed, the use of solution culture technique seems to offer the most promising means of solving some of the most important questions of plant nutrition. It may be suggested, however, that the time has arrived for the intensive study of plant growth from the standpoint of chemical metabolism. It is highly essential to learn more about the functions of different elements in the chemical system of the plant. This knowledge must be available before any satisfactory understanding of the relation of culture solutions to plant growth can be attained.

SUMMARY

A brief review is given of various precautions to be taken in interpreting the results of experiments with artificial culture solutions. Additional evidence is presented concerning the importance of taking into consideration the absorption of ions by the plant in planning such experiments.

Barley plants grown in solution, sand, and soil under identical climatic conditions, are compared with reference to total dry weight, number of tillers, grain production, etc.

A brief résumé of the present theories on physiological aspects of the soil solution is given.

Experiments are reported in which barley plants were grown in culture solutions containing phosphate in very low concentrations, maintained approximately constant. Good growth was obtained under these conditions and analogies to the soil solution are pointed out.

Attention is called to certain dissimilarities between soil solutions and artificial culture solutions, as the latter are ordinarily employed. It is concluded, however, that there is no evidence from comparative experiments that plants absorb mineral elements from the soil by a mechanism different from that operative in solution cultures.

The need for conducting more intensive chemical studies of plant growth is pointed out.

REFERENCES

- (1) Bouyoucos, G. J. 1921 The amount of unfree water in soils at different moisture contents. *In* Soil Sci., v. 11, p. 255-259.
- (2) Bouyoucos, G. J., and McCOLL, M. M. 1916 The freezing point method as a new means of measuring the concentration of the soil solution directly in the soil. Mich. Agr. Exp. Sta., Tech. Bul. 24.
- (3) BRINCHLEY, WINIFRED E. 1919 Some factors in plant competition. *In* Ann. Applied Biol., v. 6, no. 2 and 3, p. 142-170.
- (4) BROWNE, F. L. 1923. The constitution of ferric oxide hydrosol from measurements of the chlorine and hydrogen ion activities. *In* Jour. Amer. Chem. Soc., v. 45, no. 2, p. 297-321.
- (5) BURD, J. S., and MARTIN, J. C. 1923 Water displacement of soils and the soil solution. *In* Jour. Agr. Sci., v. 13, p. 265-295.

- (6) BURD, J. S., AND MARTIN, J. C. 1923 Phosphate behavior in soils. *In* Science, v. 58, no. 1499, p. 227-228.
- (7) BURGESS, P. S. 1922 The soil solution, extracted by Lipman's direct pressure method, compared with 1:5 water extracts. *In* Soil Sci., v. 14, p. 191-212.
- (8) COMBER, N. M. 1922 The availability of mineral plant food. *In* Jour. Agr. Sci., v. 12, p. 363-369.
- (9) DAVIS, A. R. 1921 The variability of plants grown in water cultures. *In* Soil Sci., v. 11, p. 1-32.
- (10) GERICKE, W. F. 1923 Further notes on the effect of extent of root systems on tillering of wheat. *In* Bot. Gaz., v. 75, p. 320-322.
- (11) GILE, F. L., AND CARRERO, J. O. 1916 Assimilation of iron by rice from certain nutrient solutions. *In* Jour. Agr. Res., v. 7, p. 503-528.
- (12) HOAGLAND, D. R. 1918 The freezing point method as an index of variations in the soil solution due to season and crop growth. *In* Jour. Agr. Res., v. 12, p. 369-395.
- (13) HOAGLAND, D. R. 1919 Relation of the concentration and reaction of the nutrient medium to the growth and absorption of the plant. *In* Jour. Agr. Res., v. 18, p. 73-117.
- (14) HOAGLAND, D. R. 1923 The absorption of ions by plants. *In* Soil Sci., v. 16, p. 225-246.
- (15) HOAGLAND, D. R., MARTIN, J. C., AND STEWART, G. R. 1920 Relation of the soil solution to the soil extract. *In* Jour. Agr. Res., v. 20, p. 381-395.
- (16) KEEN, B. A. 1919 A quantitative relation between soil and the soil solution brought out by freezing point determinations. *In* Jour. Agr. Sci., v. 9, p. 400-415.
- (17) McCALL, A. G. 1915 A new method for the study of plant nutrients in sand cultures. *In* Jour. Amer. Soc. Agron., v. 7, p. 249-252.
- (18) MC HARGUE, J. S. 1922 The rôle of manganese in plants. *In* Jour. Amer. Chem. Soc., v. 44, p. 1592-1598.
- (19) PARKER, F. W. 1921 Methods of studying the concentration and composition of the soil solution. *In* Soil Sci., v. 12, p. 209-232.
- (20) STUART, G. R., AND MARTIN, J. C. 1921 Effect of various crops upon the water extract of a typical silty clay loam soil. *In* Jour. Agr. Res., v. 20, p. 663-667.
- (21) TOTTINGHAM, W. E., AND RANKIN, E. J. 1923 Nutrient solutions for wheat. Amer. Jour. Bot., v. 10, p. 203-210.
- (22) TRELEASE, S. F., AND LIVINGSTON, B. E. 1922 Continuous renewal of nutrient solution for plants in water cultures. *In* Science, v. 55, p. 483-486.

THE LIBERATION OF POTASSIUM FROM FELDSPARS, AND OF POTASSIUM AND CARBON DIOXIDE FROM SOILS BY FERTI- LIZER AND ACID TREATMENTS¹

S. C. VANDECAYE²

Iowa Agricultural Experiment Station

Received for publication July 21, 1923

Although many cultivated soils are abundantly supplied with potassium, various field crops have often been benefited by small applications of soluble potassium fertilizers. This fact gives evidence that in many cases there is a deficiency of available potassium for maximum crop production. It also indicates the lack of understanding of the conditions necessary for the liberation of potassium in soils from its insoluble forms.

The literature on the solubility of soil potassium is highly confusing and contradictory, but investigators generally agree that certain agencies must be constantly and vigorously active in liberating unavailable soil potassium. Carbon dioxide is one of the chief agents which according to Greaves, (14) reacts with the insoluble potassium silicates to form soluble potassium carbonate.

Ames (1) believes that the salts formed as a result of the acidity produced by bacterial and chemical action effect the liberation of potassium rather than the acids themselves.

There is also the contention of Fraps (12) and Hopkins and Aumer (15) that decaying organic matter has the power to liberate insoluble soil potassium.

Other investigators claim that the application of certain fertilizers and neutral salts bring soil potassium into solution.

Most of these theories, however, are not based upon facts established by experimental data. Therefore, the need for a more complete study of the subject is plainly evident. A thorough understanding of the various agencies involved is absolutely essential in order to formulate any scheme of soil treatments which will permit profitable and economical use of the abundant supply of native soil potassium. Carbon dioxide, bacterial activities, mineral and organic acid, and decaying organic matter may all be expected to exercise some influence in making soil potassium available. The experiments reported in this paper were planned in an attempt to ascertain the relative effect of these various factors on the liberation of potassium from the insoluble supply in the soil.

¹ Part of a thesis submitted to the Faculty of the Iowa State College in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² The writer wishes to express his appreciation to Dr. P. E. Brown for the suggestions and criticism given concerning the work and the manuscript, and to Drs. Paul Emerson and H. W. Johnson for the suggestions and help given during the course of this work.

PART I

Experiments in solutions

This experiment was designed to study certain non-biological factors which might show some effect on the solubility of potassium in potassium-bearing minerals such as orthoclase, $KAlSi_3O_8$, and alunite, $K(Al(OH)_2)_3(SO_4)_2$.

The orthoclase was obtained from rocks collected locally. These were crushed and ground to pass through a sixty mesh sieve. The alunite was secured from the Mineral Products Corporation, Maryvale, Utah, and ground to the same fineness as the orthoclase. Upon analyses the orthoclase showed a total potassium content of 3.65 per cent; the alunite, 3.92 per cent. One hundred-gram portions of orthoclase or alunite, or mixtures of the two were used with varying treatments.

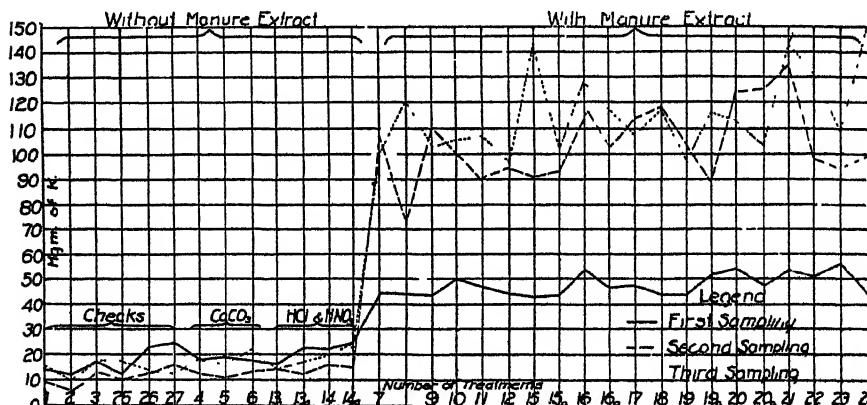


FIG. 1. GRAPH SHOWING THE EFFECT OF MANURE EXTRACT AND ACID TREATMENTS ON SOLUTIONS CONTAINING OROHOCLASE AND ALUNITE

The treatments included manure extract, lime, gypsum and certain acid treatments. The manure extract was prepared by mixing 1000 gm. of air-dry, partly decomposed barn-yard manure with 6 liters of distilled water, after standing for 4 hours the manure infusion was filtered through coarse filter paper. Fifty cubic centimeters of the filtrate were used for the treatments. This amount upon analysis showed a content of 76.8 mgm. of potassium. $CaCO_3$ and $CaSO_4$ were added in 2 gm. quantities. Hydrochloric, nitric and citric acids were used. One per cent of citric acid was added, and sufficient amounts of hydrochloric and nitric acids were used so that after the various ingredients were added the titration showed an acidity equivalent to a desired normality of the particular acid.

The mixtures of alunite and orthoclase with the various treatments were placed in shaker bottles, made up to 500 cc. with distilled water and then sterilized in the autoclave for thirty minutes at fifteen pounds pressure. In order to insure proper mixing all the bottles were shaken for 10 hours in the shaking machine before they were placed in the incubator where they were kept at a constant temperature of 25°C.

The arrangement of the experiment is shown in table 1. In order to determine the effect of sterilization, mixtures 25, 26 and 27 and those marked "a" were not sterilized. Mixtures 25, 26, 27 were prepared just previous to the first sampling for the purpose of determining the water-soluble potassium of the minerals. The samplings were taken at intervals of

four and eight weeks. At each sampling the bottles were shaken for thirty minutes. Then 100 cc. were quickly taken out with continuous stirring in order to keep the solids and liquids in the original proportions. The samples were filtered and 50 cc.-aliquots were used for water-soluble potassium determinations. The results of the three samplings calculated in milligrams on the basis of 500 cc. of solution are given in table 1. Figure 1 presents graphically the results of the three samplings.

The potassium added in the manure extract and the amount obtained before incubation of the checks are water-soluble forms and must be deducted from the total results. Since the checks did not change to any appreciable extent during the course of the experiment, the results of the three determinations on the six checks were averaged and used as the water-soluble amount present in the minerals.

Table 1 indicates that the manure extract had a large effect on the solubility of the potassium in orthoclase and alunite after 16 weeks of incubation. This supports the belief that decaying organic matter liberates potassium from potassium-bearing minerals. If the average amount liberated by the addition of CaCO_3 is deducted from the surplus due to the manure extract and CaCO_3 , and if the total average potassium present in orthoclase and alunite is taken as a mean, it is found that 0.195 per cent of the total potassium was liberated through the effect of the manure extract.

The effects of CaCO_3 and CaSO_4 were comparatively small and the data show also that the minerals were not acted upon by the acids, thus supporting the observations of McCaughy and Fry (20) who claim that acids do not affect orthoclase. However, the combined action of manure extract and acids in certain concentrations is quite remarkable. The manure extract with 1.0 *N* HNO_3 and 0.1 *N* HCl apparently had no effect, but with the weaker concentrations of HCl and HNO_3 , and with citric acid there were large effects. These are best indicated in figure 2 where averages of the result for each treatment have been plotted in the order of their increasing effect.

McCall and Smith (19) found that in composting greensand with manure and sulfur, it seemed necessary for a certain degree of acidity to be developed before any appreciable amount of potassium was made water-soluble, thus confirming the observations made here. The results are also substantiated by Ames and Boltz (2) and more recently by Ames (1), who contended, however, that the effect of the acidity was due to salts formed from the acids rather than to the direct action of the acids. This idea appears to find support in these results for the acids by themselves showed no appreciable effect on the minerals.

The behavior of the solutions during the first 4-week period of the experiment is of particular interest, because it demonstrated the phenomenon of absorption. Although the figures in the first column of the table show an apparent increase where manure extract was applied, a considerable decrease was really secured as indicated by the minus sign in the second column where the water-soluble potassium applied in the form of manure extract and feldspars was deducted. Evidently potassium bearing minerals absorb potassium from solutions. This was also observed by DeTurk (8). If this fact is taken into account the increases due to the manure extract as reported in the table

TABLE I
Water-soluble potassium liberated from orthoclase and alunite computed for 500 cc.-solutions

SAMPLE NUMBER	MATERIAL USED	TREATMENT	K IN FILTRATE 10/20/21	GAIN OR LOSS DUE TO TREATMENT	K IN FILTRATE 11/21/21	GAIN OR LOSS DUE TO TREATMENT	K IN FILTRATE 1/21/22	GAIN OR LOSS DUE TO TREATMENT	mgm.	pH
			mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	
1	Orth.		13.8	9.8	15.3					8.8
2	Alun.		11.4	Check*	10.1					7.5
3	Mix.		17.7	Check*	19.0					8.5
4	Orth.		18.2	+4.7	12.4	-1.1	18.6	+5.1		8.8
5	Alun.		19.0	+5.5	10.6	-2.9	17.3	+3.8		8.7
6	Mix.		18.0	+4.5	14.3	+0.8	22.7	+9.2		8.4
7	Orth.		45.9	-44.4	104.7	+14.4	101.9	+11.6		8.8
8	Alun.	CaCO ₃	45.9	-44.4	70.7	-19.6	120.6	+30.3		8.7
9	Mix.		43.6	-46.7	111.8	+21.5	101.6	+11.3		8.4
10	Orth.		50.2	-40.1	100.2	+9.9	107.6	+17.3		8.6
11	Alun.	CaCO ₃ + manure extract*	48.8	-41.5	91.3	+1.0	108.7	+18.4		8.5
12	Mix.		44.4	-45.9	94.1	+3.8	96.0	+5.7		8.6
13	Orth.	CaCO ₃ + 0.01 N HCl	17.7	+4.2	15.3	+1.8	15.4	+1.9		4.4
13a	Alun.		22.0	+8.5	11.9	-1.6	16.2	+2.7		3.1
14	Orth.		22.2	+8.7	16.0	+2.5	20.7	+7.2		2.4
14a	Alun.		23.8	+10.3	14.8	+1.3	23.0	+9.5		1.7
15	Alun.	CaCO ₃ + 0.01 N HCl + manure extract	42.2	-48.1	90.2	-0.1	142.5	+52.2		1.4
15a	Orth.		43.8	-46.5	93.6	+3.3	102.6	+12.3		1.5

16	Alun.	$\text{CaCO}_3 + 0.2 N \text{HNO}_3 +$ manure extract	55.7	-34.6	119.4	+29.1	129.5	+39.2	1.5
16a	Orth.		47.5	-42.8	102.9	+12.6	115.0	+24.7	1.6
17	Mix.	$\text{CaCO}_3 + 0.1 N \text{HCl} +$ manure extract	48.9	-41.4	112.0	+21.7	109.3	+19.0	1.1
18	Mix.	$\text{CaCO}_3 + 0.2 N \text{HNO}_3 +$ manure extract	44.1	-46.2	118.6	+28.3	119.8	+29.5	1.3
19	Orth.	$\text{CaCO}_3 + 0.1 N \text{HCl} +$ manure extract	44.7	-45.6	100.8	+10.5	96.4	+6.1	0.9
19a	Alun.		52.6	-37.7	88.4		117.1	+26.8	0.6
20	Alun.	$\text{CaCO}_3 + 1.0 N \text{HNO}_3 +$ manure extract	54.4	-35.9	124.7	+34.4	112.6	+22.3	0.0
20a	Orth.		47.8	-42.5	126.0	+35.7	102.6	+12.3	0.0
21	Mix.	$\text{CaCO}_3 + 1.0 N \text{HNO}_3 + 0.1 N \text{HCl} +$ manure extract	53.5	-36.8	137.7	+47.4	144.1	+53.8	0.4
22	Orth.		51.5	-38.8	99.4	+9.1	132.4	+42.1	6.3
23	Alun.	$\text{CaCO}_3 + 1$ per cent citric acid + manure extract	57.5	-32.8	95.4	+5.1	97.4	+7.1	6.3
24	Mix.		44.6	-45.7	98.3	+8.0	144.0	+53.7	6.2
25	Orth.		13.6	11.7			16.4		8.6
26	Alun.	Non-sterilized	16.0	Check	11.9	Check	12.5	Check	6.9
27	Mix.		15.6		15.6		13.8		8.4

*K added with manure extract.....76.8 mgm.

Average water-soluble K added.....13.5 mgm.

Total K added in soluble form90.3 mgm.

are by no means the maximum since a considerable part of the water-soluble potassium was undoubtedly held by the absorptive power of the minerals.

The pH values were determined in order to ascertain the relationship, if any, between the reaction of the solution and the liberation of potassium. From the figures obtained and from the graph in figure 2, it is evident that the reaction of the solution had no effect on the liberation of potassium.

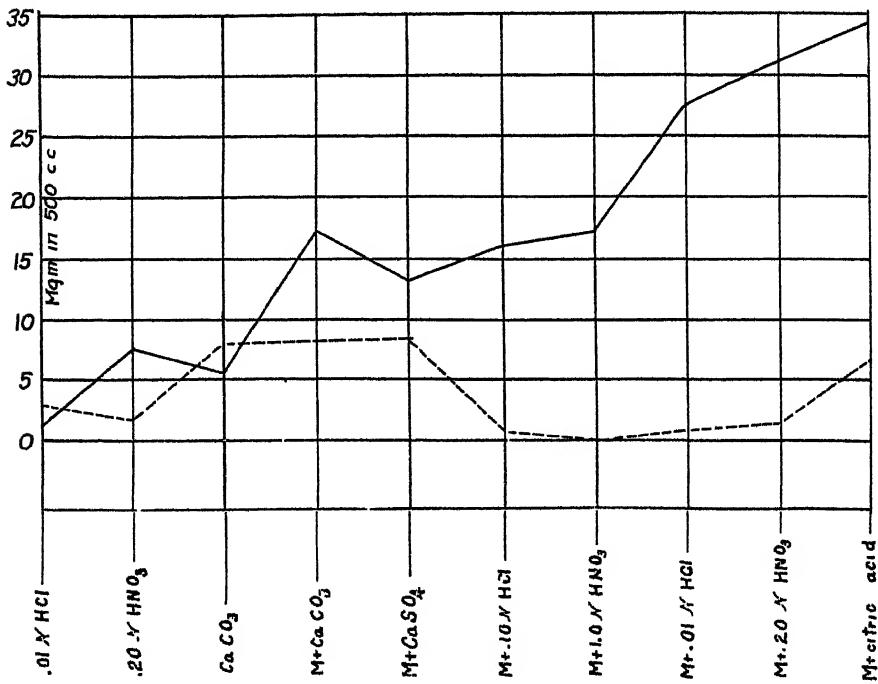


FIG. 2. GRAPH SHOWING AVERAGE INCREASE IN WATER-SOLUBLE POTASSIUM AND pH VALUES OF THE DIFFERENT TREATMENTS AFTER SIXTEEN WEEKS

— water-soluble potassium; - - - pH value

PART II

Experiments in soil

Carrington loam secured from plot 107 of the humus plots of the Iowa Station was used as the basis of these experiments. This plot has been kept fallow since 1908 and has received no treatment whatever. A sample of the soil to a depth of eight inches was taken, air dried, and sieved. The total potassium content was 30,588 pounds per acre of 2,000,000 pounds of surface soil, and the lime requirement as determined by the Truog method was two tons. Five hundred grams of air-dry soil were thoroughly mixed with the various materials in bottles as in part 1, and distilled water was added to obtain the optimum moisture content, which was 25 per cent. For the alundum and quartz treatments, the optimum moisture was 11 per cent. With the air-dried manure and clover hay applications, it was necessary to add their equivalent weight in water in order to bring those treatments up to

the optimum moisture. During the progress of the experiments, the moisture content was maintained by regulating the moisture content of the air which was continually passed over the soil. Air drawn through a solution of 30-35 per cent H₂SO₄ contained approximately the amount of moisture required to keep the soil at the optimum.

The carbon dioxide determinations were made according to the method of Potter and Snyder (23). Since sterile air was imperative for part of the experiments, it was necessary to make a slight modification in the apparatus. An absorption tower packed with sterile cotton was placed between A and B, and also between C and D shown on figure 1, page 282 in Potter and Snyder's report. The towers filled with cotton were sterilized in the autoclave every three or four weeks in order to destroy any organisms which might enter.

The carbon dioxide was determined at intervals of one, three, five, seven days, and every seventh day thereafter. The soils were sterilized three time in the autoclave at 15 pounds pressure for three hours with intermissions of 36 hours each. This was found to be necessary to destroy all microorganisms and spores. The apparatus was of necessity sterilized in several parts which had to be reassembled before the experiment could be started. This operation naturally increased the possibilities for contamination. During the course of the experiment, several instances of such contaminations were observed but in each case the contaminated bottles were resterilized and no further difficulties were encountered.

At the end of the experiments the sterilized soils were tested for bacterial contents, and all proved to be sterile.

Series 1

This series was planned primarily to ascertain whether results obtained in part 1, could be duplicated in soils. Orthoclase was applied to the soil in portions of 20 gm. per treatment. Manure was used at the rate of 8 tons per acre and acid phosphate at the rate of 400 pounds. CaCO₃ and CaSO₄ were applied at the rate of 3 tons per acre. The lime requirement was regulated by adding a certain amount of HCl which would give approximately the required acidity conditions; then the final adjustment was determined by the Truog acidity test. The treatments are shown in table 2.

Each treatment was prepared in six duplicates, two of which were not sterilized, two were sterilized, but not kept sterile, and two were sterilized and kept sterile. The duration of the experiments was 8-11 weeks, but for convenience all calculations for total carbon dioxide are based on 10 weeks. The results of the first titrations are not included in the calculations because it was thought that the carbon dioxide obtained was largely accumulated and not formed as a result of the treatment. The results showing the total carbon dioxide production, the water-soluble potassium, and the pH values are given in table 2 and plotted in figure 3.

Although the manure extract appeared to be the most effective single factor in the experiment with potassium bearing minerals in part 1, such was not the case with manure in this test. The suggestion might be made that manure and manure extract act differently. This was determined by conducting a separate experiment to compare the effect of manure with that of manure extract. The treatments were prepared in duplicates similarly to the sterile set in series 1. Four grams of manure and 50 cc. of manure extract were used as a basis for comparison. The results secured in eight weeks are given in table 3 from which it can readily be seen that the difference, which is slightly in favor of the manure extract, is not large enough to be significant.

The application of manure in series 1 was relatively small and although there was an apparent increase in soluble potassium, its effect was not nearly so outstanding as that observed in Part 1.

It is interesting to note that the addition of orthoclase resulted in a slight increase in water-soluble potassium both when applied alone and when in com-

bination with CaSO_4 . This would indicate that the potassium in ground orthoclase is more readily attacked than the soil potassium. This statement finds support in the experiments of Magnus (17) and Hopkins and Aumer (15).

TABLE 2

Water-soluble potassium, total carbon dioxide and pH values of sterile and non-sterile soils of series 1, calculated from averages of duplicates

SAMPLE NUMBER	SOIL TREATMENT	NOT STERILIZED			STERILIZED BUT NOT KEPT STERILE			STERILIZED AND KEPT STERILE		
		K per acre	CO ₂ in 500 gm. soil	pH	K per acre	CO ₂ in 500 gm. soil	pH	K per acre	CO ₂ in 500 gm. soil	pH
		lbs.	gm.		lbs.	gm.		lbs.	gm.	
1	Check	57.9	1.724	5.2	82.1	2.407	5.0	67.6	0.934	5.1
2	Orthoclase	64.4	1.920	5.3	95.0	2.473	5.1	70.8	1.183	5.2
3	Manure	69.2	2.625	5.5	91.8	2.678	5.3	96.6	1.260	5.2
	<i>Manure</i>									
4	CaCO ₃ Orthoclase	72.4	2.451	6.6	128.9	2.422	5.3	93.4	0.903	6.1
5	CaCO ₃ + Orthoclase + acid phos.	69.2	2.658	6.6	159.3	2.607	5.4	86.9	0.799	5.6
6	CaSO ₄	99.8	2.190	5.1	179.2	2.454	5.1	112.7	0.844	5.1
7	CaSO ₄ + Orthoclase	112.7	2.367	5.2	135.3	2.488	5.1	125.5	0.907	5.1
	<i>Orthoclase and HCl to adjust to lime req. of 3 tons</i>									
8		83.7	1.914	4.9	103.1	2.524	4.7	96.6	0.995	4.6
9	Manure	109.5	2.005	4.9	160.8	2.507	4.7	115.9	1.010	4.7
10	Manure + acid phos.	138.5	2.441	4.6	157.9	2.474	4.7	143.3	1.107	4.7
	<i>Orthoclase and HCl to adjust to lime req. of 5 tons</i>									
11		107.9	1.977	4.1	172.4	2.563	4.1	149.8	0.992	4.4
12	Manure	186.8	1.972	4.2	164.3	2.536	4.2	220.7	0.991	3.9

TABLE 3

Water-soluble potassium and total carbon dioxide from soil treated with manure and manure extract, calculated from averages of duplicates

TREATMENT	K PER ACRE	TOTAL CO ₂ IN 500 GM. SOIL	
		lbs.	gm.
Manure.....	101.4		1.453
Manure extract.....	104.7		1.493

The relatively small application of CaSO_4 resulted in a decided increase in water-soluble potassium in both sterile and non-sterile soils. Although these results support the observations of McMiller (21) and Bradley (4) it should not be overlooked that negative results might be secured if the treatment were

applied to soil types derived from orthoclase bearing rocks as suggested by Briggs and Breazeale (5). The possible cause of the beneficial effect of CaSO_4 as suggested by Bradley (4) is that the cation of the gypsum is fixed by the soil and a corresponding quantity of potassium goes into solution to form K_2SO_4 . The conclusion reached by Dussere (9) who claimed that the liberation of potassium from soils through the applications of gypsum, ammonium sulfate, and calcium superphosphate was due to the acidity resulting from those fertilizers does not find much support in the results obtained in these experiments, since the pH value was practically unchanged by the CaSO_4 treatments. Bradley's suggestion seems more plausible, although no actual proof can be given here.

Probably the most outstanding data in this experiment are those showing the action of the acids on the liberation of potassium. It will be recalled from part 1, that the direct action of acids had no effect on the potassium bearing minerals, but when applied in combination with manure extract they produced decided effects upon the solubility of potassium. This soil contains considerable organic matter and hence an effect similar to that observed in part 1 could easily be produced. Again, the theory of Ames and Boltz (2) and of Ames (1), as to the action of salts of acids may be considered to be supported by the results of this experiment, but in this theory, the effects of colloids in the soil have been overlooked.

The striking coincidence that the increase in water-soluble potassium was invariably associated with a corresponding increase in hydrogen-ion concentration leads to another possibility suggested by the work of Gordon and Starkey (13). They showed that a small change in hydrogen-ion concentration around pH 7 was followed by a large decrease in the absorption of potassium by silica gel and that when the hydrogen-ion concentration was further increased the potassium became correspondingly less absorbed and consequently more available. Their results seem to be in agreement with those reported in tables 1 and 2, with the exception of the treatments which have a hydrogen-ion concentration of less than pH 1.0.

If pure, artificial silica gels manifest a lesser absorptive capacity for potassium under acid conditions, it is not unlikely that the silica colloids and gels in the soil exhibit a similar behavior. Silica colloids and gels according to Ostwald (22) constitute one of the four most important classes of soil colloids. Consequently they were very likely present both in the soil and in the minerals used in these experiments. Furthermore, they were probably present in the soil which McCall and Smith, Ames and Boltz, and Ames used. Although those investigators did not determine the hydrogen-ion concentration, they found an appreciable increase of water-soluble potassium only under acid conditions. These striking coincidences would certainly lead to the suggestion that possibly the condition of the colloidal material in general and of silica gels in particular are to a large extent responsible for the amount of potassium obtained in water extracts.

The results in table 2, obtained in sterilized soil subsequently exposed to non-sterile air, show the highest amounts of water-soluble potassium and carbon dioxide. Sterilization was undoubtedly responsible for part of the increase in water-soluble potassium but it will be noticed that the soil which was kept sterile throughout the experiment gave lower results in all treatments except in no. 18. No explanation can be offered for this exception.

The difference then between the sterilized soil which was exposed to non-sterile air and that which was kept sterile must be due to some factor other than sterilization. The carbon dioxide production of the former was about three times greater than that of the latter, and considerably greater than that of the unsterilized soil. This large carbon dioxide production was probably due to the action of molds which formed an exceptionally dense growth on all the sterilized soils subsequently exposed to non-sterile air. It seems that in the absence of competing organisms those molds were very active in the decomposition of organic matter, with the result that decidedly increased amounts of carbon dioxide and slightly increased amounts of water-soluble potassium were produced. The relation of carbon dioxide production to the liberation of potassium will be considered in series 2.

Series 2

The purpose of this series was to determine the effect of relatively large amounts of organic matter on the liberation of soil potassium. Soil and orthoclase were used in the same manner as in series 1. Since the absorptive power of soil offers the chief difficulty in water-soluble potassium determinations, alundum, which is a non-absorbent and inert material, was introduced into the series in order to give an estimate of the amount of water-soluble potassium absorbed by the soil during the course of the experiment. Quartz, although absorbing a small amount of potassium, was used in comparison with alundum. CaCO_3 and acid phosphate were applied to study their effect when combined with large amounts of organic matter. CaCO_3 was used at the rate of four tons per acre and acid phosphate at the rate of 1000 pounds per acre. When alundum and quartz were used the potassium applied consisted in a mixture of 50 gm. of orthoclase and 50 gm. of alunite.

Manure was added at the rate of 16 and 32 tons per acre and clover hay at the rate of 4 and 12 tons per acre. The manure contained 1.071 per cent or 21.42 pounds of total potassium per ton, and the clover hay 0.981 per cent or 19.62 pounds per ton. As a large part of this potassium is in a soluble form, the total amount was deducted from the final results in table 5.

During the second week of the experiment a leak in the apparatus of the sterile set, caused contamination of all the bottles with the exception of sample 19-a. The contaminated bottles were resterilized, but separate analyses were made of the one that was not contaminated. The arrangement of the test is shown in table 4.

Each treatment was prepared in quadruplicate, two kept sterile and two non-sterile. The duration of the experiment was 11 weeks for the sterile and 12 weeks for the non-sterile. For convenience, the total carbon dioxide was calculated on the basis of 10 weeks. The results of the water-soluble potassium, the total carbon dioxide and the pH values are reported in table 4. The amount of water-soluble potassium added in the form of manure and orthoclase is not taken into account. According to Fraps (11) the water extract from the soil does not necessarily represent the solubility of the potassium minerals exposed to the action of the solvent, but the difference between the potassium dissolved by the solvent and the soluble potassium absorbed by the soil. This absorbed potassium of the soil is

TABLE 4

Water-soluble potassium, total carbon dioxide, and pH value from sterile and non-sterile soils of series 2, calculated from averages of duplicates

SAMPLE NUMBER	TREATMENT				NOT STERILIZED				STERILIZED AND KEPT STERILE		
	Manure	CaCO ₃	Acid phosphate	Clover hay	K per acre	Citrate soluble K per acre	CO ₂ in 500 gm. soil	Reaction	K per acre	CO ₂ in 500 gm. soil	Reaction
					lbs.	lbs.	gm.	pH	lbs.	gm.	pH
13	8	2			125.5	505.2	3.207	6.8	188.2	2.710	4.8
14	16	2			164.1	553.4	3.435	7.0	271.9	2.665	6.0
15	16	2	0.25		202.9	460.1	3.350	6.8	328.2	2.854	5.6
16	16				199.7	637.1	3.297	6.1	352.3	2.877	4.9
17				2	80.5	405.4	2.714	4.9	143.2	2.469	4.6
18				6	167.5	421.5	3.231	4.8	189.8	2.774	4.4
19		2		6	165.9	341.1	3.140	6.3	204.3	2.146	5.6
19a									151.2	1.661	
20		2	0.25	6	180.4	370.0	3.085	6.3	165.7	2.075	5.3
21	8*				325.0	431.2	2.162	8.9	350.7	1.835	7.9
22	8*	2			327.0	617.8	2.331	9.1	331.4	1.991	9.1
23	8†				304.1		2.423	8.2	297.6	1.772	7.3

* Alundum added.

† Quartz added.

TABLE 5

Increase or decrease in water-soluble potassium due to treatment, after deduction of soluble amounts added in the form of organic matter and orthoclase

SAMPLE NUMBER	TREATMENT				NOT STERILIZED				STERILIZED AND KEPT STERILE				
	Manure	CaCO ₃	Acid phosphate	Clover hay	K per acre	K added	Decrease	K second extract	Increase or decrease	K per acre	K added	Increase or decrease	K second extract
					lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	
13	8	2			125.5	352.5	-127.0			188.2	352.5	-164.3	
14	16	2			164.1	697.2	-533.1			271.9	697.2	-426.3	
15	16	2	0.25		202.9	697.2	-494.3			328.2	697.2	-369.0	
16	16				199.7	697.2	-497.5	115.8	-381.7	352.3	697.2	-344.9	
17				6	80.5	89.2	-8.7			143.2	89.2	+54.0	
18				6	167.5	246.2	-78.7			189.8	246.2	-56.4	
19		2		6	165.9	246.2	-80.3			204.3	246.2	-41.9	
20		2	0.25	6	180.4	246.2	-65.8			165.7	246.2	-80.5	
21	8*				325.0	396.7	-71.7	80.4	+8.7	350.7	396.7	-46.0	98.1
22	8*	2			327.0	396.7	-69.0	78.8	+9.0	331.4	396.7	-65.3	99.7
23	8†				304.1	396.7	-92.6			297.6	396.7	-99.1	

* Alundum added.

† Quartz added.

only very slowly acted upon by water. Vanatta (27) found that boiling twice for a period of two hours failed to release any considerable amounts of absorbed potassium.

It was found necessary in series 2 to make a second water extract on the two sterile and non-sterile alundum samples, in order to remove the potassium held mechanically. A second extract was also made of one of the treated soils. The results of this second analysis, together with the increase or the decrease of water-soluble potassium after deduction of that added in the form of minerals and manure are reported in table 5. The water-soluble potassium of the minerals was taken from the average amount found in part 1.

The results in table 4 show an apparent increase in water-soluble potassium corresponding roughly to the increase in organic matter added. However, when the soluble potassium added in the form of manure, clover hay and orthoclase was subtracted as shown in table 5, there was a decrease in water soluble potassium throughout the series. This decrease was undoubtedly due to the absorptive power of the soil.

According to Anderson (3) and his associates, 95 per cent of the absorption of potassium in soils is due to colloidal material. This absorbed potassium is only very slowly given up by the action of water. McCall, Hilderbrandt and Johnston (18) found that the curve showing the amounts of potassium removed by successive washings of a soil through which a solution of KCl had been percolated was almost a straight line. It is also possible that some of the soluble potassium was held in loose combination with small mineral particles. That would probably account for the relatively large amounts of potassium obtained in the second extract, notably the extract of sample 16. It would be noted that the sum of the two extracts of the sterile and non-sterile alundum treatments given in table 5, do not necessarily represent the total potassium that was rendered soluble in the experiment. The minerals and the manure very likely contained materials which formed colloidal complexes capable of absorbing potassium. Hence, in view of the fact that the absorption factor was not considered, and that, only 95.1 per cent of the potassium in the manure was water-soluble, the increases due to the action of manure indicated in table 5, are probably too low.

It is of interest to note that the positive results with the liquid medium in part 1 were almost duplicated with the alundum medium but that the soil itself gave negative results.

The official method with neutral ammonium citrate was used on the unsterilized treatments of series 2, in an attempt to ascertain the amount of absorbed potassium. The results are reported in column 3 of table 4, and since they show no indication of the quantities of absorbed potassium in those soils the method was discontinued.

The result reported in table 5, for the second extract of sample 16, might lead to the belief that repeated water extractions would give satisfactory results, but it should not be overlooked that the amount reported was far from the total amount absorbed. Furthermore, at least part of the potassium in the extract was probably held loosely around small particles instead of in the absorbed form. Schreiner and Failyer (24) passed a solution of KCl through various

soils and by continuous percolation of water, obtained amounts of potassium which showed no indications of the quantity absorbed by the soil. The more recent work of McCall (18) and his associates showed that only very small amounts of absorbed potassium were given up in repeated water extractions.

All this goes to show that the chief difficulty in the determination of soluble soil potassium lies unquestionably in the absorptive power of the soil colloids and that other methods differing from the water extract method should be resorted to.

The addition of calcium carbonate and acid phosphate showed no appreciable effect on the liberation of potassium and the production of carbon dioxide. The slight differences reported in table 4 are easily within the limits of experimental error.

The application of organic matter in the form of manure and clover hay increased the carbon dioxide production in the soil. Comparatively small applications of clover hay appeared to have a decided effect on the carbon dioxide production. The maximum production for the Carrington loam seemed to be reached with applications of 16 tons of manure per acre. Larger applications did not increase the carbon dioxide production to any extent. More carbon dioxide was produced in the soil than in quartz, due to the decomposition of the organic matter in the soil. There seemed to be a close relationship between the carbon dioxide production and the liberation of potassium as indicated by the water-soluble method. The curves in figure 3, show that this relationship holds for the soils, but not for the alundum and quartz due probably largely to the absorption factor.

The sterilization of soils would naturally be expected to result in a decided decrease in carbon dioxide production since all bacterial action is stopped. The investigations of Deherain and Demoussy (7) Wollny (28) and Severin (25) indicated that comparatively little carbon dioxide was produced in sterile soils and that the ratio between the amounts produced in sterile and non-sterile soils was 1:10.

The results of this experiment as reported in table 4 showed that considerable carbon dioxide was produced in the sterile soils. In fact, the quantities produced amounted to approximately 50 per cent of that in the non-sterile duplicates of series 1 and approximately 70-75 per cent of the non-sterile duplicates of series 2. The reason for the higher results in series 2, is found in the fact that all the bottles except one were resterilized. Heat and pressure in the autoclave seemed to have an effect on the production of carbon dioxide as well as on the soluble potassium of soils. The results in table 6, show that sample 19 produced approximately 24 per cent more carbon dioxide than its duplicate which did not get contaminated. Therefore, if 24 per cent of the carbon dioxide were subtracted from the results of the sterile part in series 2, the curves in figure 3 would show approximately the same relationship in both series. It seems that those corrected results would represent largely amounts of carbon dioxide produced by purely chemical action.

The contention of Stoklasa and Ernest (26) that the two sources of carbon dioxide in soil are bacterial activities and plant root action does not find much support in the results of these experiments, because neither bacteria nor plant roots were present. It is true that the effect of sterilization may have started the breaking down of the organic matter so that hydrolysis and catalytic action could be more effective. However, the production of carbon dioxide in the sterile soils occurred similarly to that in non-sterile soil; the first four or five weekly determinations gave the largest quantities and thereafter a gradual decrease was noticeable.

TABLE 6

Total water-soluble potassium and carbon dioxide of sample 19 sterilized two times and of its duplicate sterilized once

SAMPLE NUMBER	K PER ACRE	CO ₂ IN 500 GM. SOIL
	lbs.	gm.
19 sterilized twice.....	204.3	2.146
19-a sterilized once.....	151.2	1.661

TABLE 7

*Water-soluble potassium per acre and freezing point depression of soils sterilized once, compared with those sterilized twice**

TREATMENT	STERILIZATION	TOTAL WATER- SOLUBLE POTASSIUM	FREEZING POINT DEPRESSION	INCREASE <i>per cent</i>
			lbs.	
Sterilized twice, 16 T.M.† applied	Non-sterile	170.5	0.252	36.7
	Sterile	233.3		
Check sterilized once	Non-sterile	56.3	0.708	25.7
	Sterile	70.8		
Optimum moisture, sterilized twice, 16 T.M. applied	Non-sterile		0.252	25.5
	Sterile		0.708	
Soil extract, sterilized once, 16 T.M. applied	Non-sterile		0.027	25.0
	Sterile		0.036	

* Sterilization was done as described in the experimental procedure of part 2.

† T.M.—Tons of manure.

The water-soluble potassium was increased invariably in all sterilized treatments, yet the carbon dioxide production was decreased 50 per cent or more. The results show that there was absolutely no relation between the carbon dioxide production and the liberation of potassium in the soil and that the sterilization caused large amounts of potassium to become water-soluble.

Lyon and Bizzell (16) found that sterilized soil yielded decidedly more soluble potassium and other plant food. The results in table 7, show some interesting relations between the soluble potassium and the total salts in solu-

tion in the sterile and non-sterile soils. One sterilization resulted in an increase of 25.7 per cent in water-soluble potassium, and 25.0 per cent in the freezing point depression of the soil solution. Two sterilizations caused an increase of 36.7 per cent in the water-soluble potassium and 25.5 per cent in the freezing point depression of the soil solution. It appears, therefore,

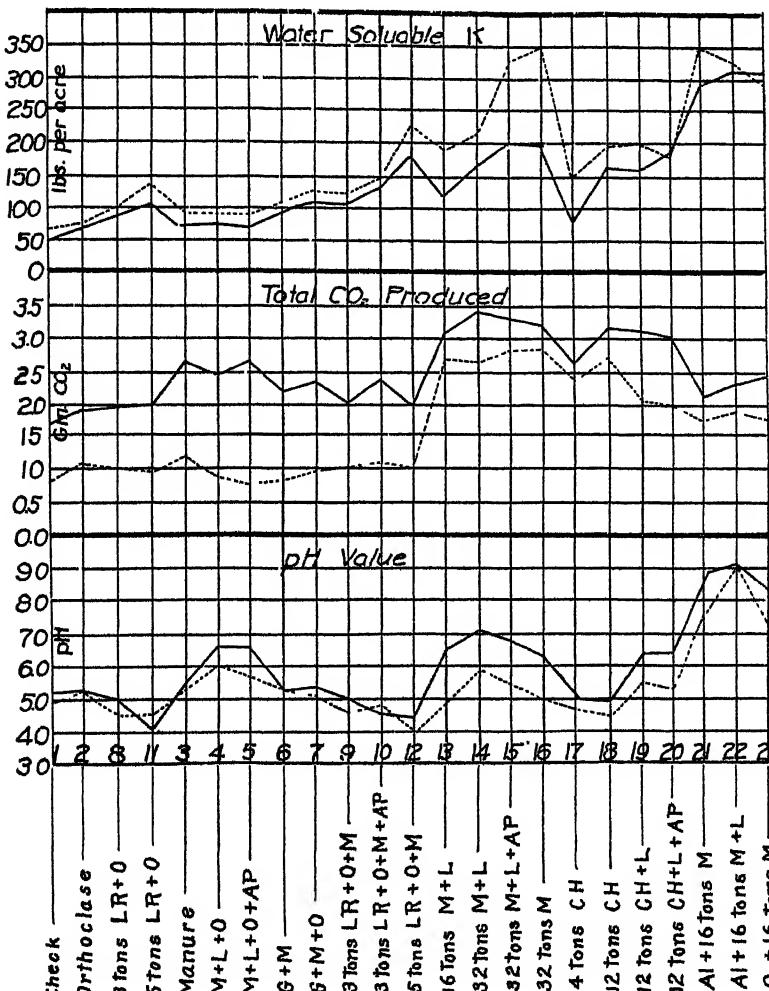


FIG. 3. GRAPH SHOWING THE RELATION BETWEEN THE PRODUCTION OF CARBON DIOXIDE AND THE LIBERATION OF WATER-SOLUBLE POTASSIUM IN STERILE AND NON-STERILE SOILS, AND THE RELATION OF THE pH VALUE TO THE PRODUCTION OF CARBON DIOXIDE, OR THE LIBERATION OF WATER-SOLUBLE POTASSIUM IN THE SAME SOILS

— non-sterile; —— sterile; M, manure; L, CaCO₃; G, CaSO₄; CH, clover hay; O, orthoclase; Al, alunite; Q, quartz; AP, acid phosphate; LR, lime requirement.

that heat and pressure have a decided effect on the solubility of potassium and other plant foods.

Comber (6) found that heat caused the dehydration and breaking up of colloidal aggregates which exposed a larger surface to the solvent agencies and resulted in a larger quantity of soluble material. It is reasonable to suppose that heat and pressure in sterilization have a similar effect and, consequently, the higher yields of water soluble potassium from the sterilized soils shown graphically in figure 3 are only apparent. A correction of 25 per cent for series 1, and 36.7 per cent for series 2, should be made before the results can be compared. Such a correction would show that the amount of water-soluble potassium in the sterile soils was approximately the same as in the non-sterile soils. It appears then that the production of carbon dioxide has no direct relation to the amount of water-soluble potassium.

The reaction of the soils seemed to be affected to a slight degree by sterilization. The pH values given in tables 2 and 4 indicate that for some unknown reason nearly all the sterilized soils gave a slightly higher hydrogen-ion concentration than the non-sterile soils. The soil reaction as a whole, however, proved to be of minor importance in these experiments. The curves in figure 3, which represent the pH values of all the treatments in part 2, show absolutely no relation between these values and the liberation of water-soluble potassium or the production of carbon dioxide.

SUMMARY

These tests permit of certain conclusions. The fact that the absorptive power of colloidal matter prevented the complete removal of all the liberated potassium by water extracts indicates that the amounts recovered with the water-soluble method are not as large as they should be but they are satisfactory for comparative purposes.

1. A manure extract and a combination of manure extract and acids in moderate concentrations gave a decided increase in water-soluble potassium from finely ground orthoclase and alunite in water solutions. Sterilization and the addition of acids, calcium carbonate, and calcium sulfate did not increase the water-soluble potassium of the same minerals.
2. The application of relatively small amounts of calcium sulfate to Carrington loam caused an increase in water-soluble potassium while calcium carbonate and acid phosphate did not.
3. The action of contaminating forms, consisting largely of molds, resulted in a decided increase in carbon dioxide and a smaller increase in water-soluble potassium in sterilized soil.
4. Organic matter such as manure and clover hay, and a combination of acids and organic matter applied to sterile and non-sterile soil resulted in an increase of water-soluble potassium. This increase, due to the absorptive power of the soil colloids, was less than the amount of soluble potassium applied in the form of manure and clover hay.

5. The production of carbon dioxide did not prove to be an index of the quantity of water-soluble potassium liberated. The maximum carbon dioxide production was secured with applications equivalent to 16 tons of manure per acre.

6. The carbon dioxide produced in sterile soils was approximately 50 per cent of that obtained in the non-sterile duplicates.

7. Sterilization resulted in a decided increase in the concentration of the soil solution and in the amount of water-soluble soil potassium. It also resulted in a slight increase in the hydrogen-ion concentration of the soil.

8. The reaction of the soil showed no relation to the carbon dioxide production or to the liberation of potassium, but there seemed to be some indication that a hydrogen-ion concentration less than pH 6 decreased the potassium-absorbing power of soil colloids.

REFERENCES

- (1) AMES, J. W. 1921 Solvent action of nitrification and sulfocification. *Ohio Agr. Exp. Sta. Bul.* 351.
- (2) AMES, J. W., AND BOTZ, G. M. 1919 Effect of sulfocification and nitrification on potassium and other soil constituents. *In Soil Sci.*, v. 7, no. 3, p. 183-195.
- (3) ANDERSON, M. S., FRY, W. H., GILL, P. L., MIDDLETON, H. E., AND ROBINSON, W. O. 1922 Absorption by colloidal and non-colloidal soil constituents. *U. S. Dept. Agr. Bul.* 1122.
- (4) BRADLEY, E. C. 1910 On reaction of lime and gypsum on some Oregon soils. *In Jour. Indus. and Engin. Chem.*, v. 2, no. 12, p. 529-30.
- (5) BRIGGS, L. J., AND BREAZEALE, J. F. 1917 Availability of potash in certain orthoclase bearing soils as affected by lime and gypsum. *In Jour. Agr. Res.*, v. 8, no. 1, p. 21-28.
- (6) COMBER, N. M. 1922 The flocculation of soils. *In Jour. Agr. Sci.*, v. 12, p. 372-86.
- (7) DEHERAIN, P. P., AND DEMOUSSY, E. 1896 Production d'acide carbonique par simple action chimique. *In Compt. Rend. Acad. Sci. (Paris)*, v. 123, no. 5, p. 278-83.
- (8) DETURK, E. 1919 Potassium bearing minerals as a source of potassium for plant growth. *In Soil Sci.*, v. 8, p. 269-99.
- (9) DUSSERRE, C. 1900 Investigation de la potasse dans la terre cultivee. *In Ann. Agr. Suisse*, v. 1, no. 2, p. 66-67.
- (10) FRAPS, G. S. 1904 Factors of availability of potash and phosphoric acid in soils. *In Science*, n. s., v. 19, no. 481, p. 443.
- (11) FRAPS, G. S. 1912 The active potash of the soil and its relation to pot experiments. *In Texas Agr. Exp. Sta. Tech. Bul.* 145.
- (12) FRAPS, G. S. 1916 The effect of additions on the availability of soil potash and the preparation of sugar humus. *In Texas Agr. Exp. Sta. Bul.* 190.
- (13) GORDON, N. E., AND STARKEY, E. B. 1922 Influence of soil colloids on the availability of salts. *In Soil Sci.*, v. 14, p. 1-7.
- (14) GREAVES, J. E. 1922 Agricultural Bacteriology, p. 180. Lea and Febiger, Phila.
- (15) HOPKINS, C. C., AND AUMER, J. P. 1915 Potassium from the soil. *In Ill. Agr. Exp. Sta. Bul.* 182.
- (16) LYON, T. L., AND BIZZELL, J. A. 1910 Effect of steam sterilization on the water-soluble matter in the soils. *In N. Y. (Cornell) Agr. Exp. Sta. Bul.* 275.
- (17) MAGNTUS, G. 1850 Ueber die Ernahrung der Pflanzen. *In Jour. Prakt. Chem.*, v. 50, p. 65-75.

- (18) McCALL, A. G., HILDERBRANDT, F. M., AND JOHNSON, E. S. 1916 The absorption of potassium. *In* Jour. Phys. Chem., v. 20, p. 51-63.
- (19) McCALL, A. G., AND SMITH, A. M. 1920 Effect of manure sulfur composts upon the availability of the potassium of greensand. *In* Jour. Agr. Res., v. 19, p. 239-56.
- (20) McCaughey, W. J., AND FRY, W. H. 1913 The microscopic determination of soil-forming materials. *In* U. S. Dept. Agr. Bur. Soils Bul. 91.
- (21) McMILLER, P. R. 1918 Influence of gypsum upon the solubility of potash in soils. *In* Jour. Agr. Res., v. 14, no. 1, p. 61-66.
- (22) OSTWALD, W., AND FISCHER, M. F. 1922 Theoretical and Applied Colloid Chemistry, p. 161. Wiley & Son, N. Y.
- (23) POTTER, R. S., AND SNYDER, R. S. 1916 Carbon dioxide production in soils and carbon and nitrogen changes in soils variously treated. *In* Iowa Sta. Res. Bul. 39.
- (24) SCHREINER, O., AND FAILYER, G. H. 1905 The absorption of phosphates and potassium by soils. *In* U. S. Bur. Soils Bul. 32.
- (25) SEVERIN, S. A. 1910 Die Mobilisierung der Phosphorsaure des Bodens unter dem Einflus der Lebenstätigkeit der Bacterien. *In* Centbl. Bakt. (etc.) Abt. 2, v. 28, p. 561.
- (26) STOKLASA, J., AND ERNEST, A. 1911 Ueber den Ursprung die Menge und die Bedeutung des Kohlendioxyds im Boden. *In* Ztschr. Zuckerindus. Böhmen, v. 31, p. 291-307.
- (27) VANATTA, E. E. 1915 Report on availability of potash. *In* Jour. Assoc. Off. Agr. Chem., v. 1, p. 24-25.
- (28) WOLLNY, E. 1897 Die Zersetzung der organischen Stoffe, p. 20-21. Carl Winter, Heidelberg.

THE LEACHING OF ALKALI SOIL

J. E. GREAVES, C. T. HIRST AND YEPPEA LUND

Utah Agricultural Experiment Station

Received for publication August 29, 1923

The following methods have been used with varying degrees of success for reclaiming alkali soil or for alleviating temporarily its ill effects: (*a*) plowing the surface soil and maintaining the alkali at a low level by systematic use of irrigation water; (*b*) quickly flooding the soil and then draining it; (*c*) removing the alkali from the surface by scraping; (*d*) growing alkali-tolerant crops; (*e*) neutralizing the alkali by chemicals or organic matter. These methods have been practiced with varying degrees of success. But in the majority of cases where the alkali has accumulated in quantities sufficient to materially interfere with plant growth they can be considered as mere temporary expedients. The only permanent procedure is the installation of underground drains. In some soils and with specific salts this is highly successful, whereas with other soils or with different salts it is either only a partial success or a total failure. The failure is often due to the imperviousness of the soil to water which makes leaching impossible. At times the soil is readily leached of its alkali content but is barren for a number of years after the leaching.

This work was undertaken to determine the rapidity with which the various salts leach from different soils, the quantity of plant-food which is taken from the soil in the leaching, and the chemical and biological changes which have resulted from the action of the various salts upon the soil and their removal. In this paper we shall deal with the chemical phase of the subject and in a subsequent article the biological phase will be considered.

PLAN OF EXPERIMENT

Two-gallon jars, provided with a half-inch hole near the lower edge were used. Into these holes were fitted rubber stoppers and glass tubes so that all drainage water could be collected, measured, and analyzed. A small quantity of glass wool was placed over the opening and the bottom of the jar was covered to a depth of two inches with fine gravel. This was covered with a layer of glass wool. Sufficient soil to fill the pots was mixed with the requisite salts, packed into the pots, and the moisture content made to 20 per cent. Some pots contained untreated, natural alkali soils. The salts treatments were as follows:

- 2 per cent sodium chloride
- 2 per cent sodium sulfate
- 2 per cent sodium carbonate
- 1 per cent sodium chloride plus 1 per cent sodium sulfate
- 1 per cent sodium chloride plus 1 per cent sodium carbonate
- 1 per cent sodium sulfate plus 1 per cent sodium carbonate
- ½ per cent each sodium chloride, sodium sulfate, and sodium carbonate

In one of the natural alkali soils the chlorides predominated, in another the sulfates, and in still another the carbonates. Eight pots were used for each treatment, six of which were leached and the other two unleached; results are reported as averages of six or two pots, respectively. Both the natural and artificial alkali soils were permitted to stand for two months with a moisture content of 20 per cent before leaching so that the reactions which were going to occur would tend toward equilibrium. At the close of this period six pots in each series were leached. This was done by keeping a "water head" on them as near constant as possible. All drain water was collected and the following data taken:

Time necessary to leach each specific salt from the soil

Quantity of water required for the leaching

Analysis of approximately every 2000 cc. of the drainage water for the specific salts added and for phosphorus, potassium, nitrogen, and carbon.

COMPOSITION OF SOIL USED

The work was conducted on four different soils:

1. From the College Farm just east of the Plant Industry Building
2. From Corinne
3. From Benson Ward
4. From Richland Acres

Soil 1 was a good productive soil and was made unproductive by the addition of the salts listed above. Soils 2, 3 and 4 were natural alkali soils containing sufficient alkali to prevent the growth of all vegetation except a few salt-tolerant plants. The physical analyses of the four soils as determined by the Yoder (16) elutriator are given in table 1.

TABLE 1
Physical composition of soils

CONSTITUENTS	COLLEGE	CORINNE	BENSON	RICHLAND
	FARM SOIL	SOIL	WARD SOIL	ACRES SOIL
	per cent	per cent	per cent	per cent
Sand.....	36.6	17.5	42.5	4.8
Fine sand.....	30.6	17.3	20.9	29.6
Coarse silt.....	18.8	28.5	19.0	27.0
Medium silt.....	6.0	15.9	3.8	13.1
Fine silt.....	2.3	5.3	2.3	10.2
Clay.....	3.5	7.4	6.1	9.4
Moisture, soluble salts, and loss.....	2.2	8.1	5.4	5.9

Soils 1 and 3 are sandy loams whereas soils 2 and 4 are fine sandy loams. These soils should be more difficult to leach than a sand and much less difficult than a tight or heavy clay. However, they represent approximately the composition of the average alkali soil. Therefore the results obtained in this work should give a fair idea of what may be expected in the field with the various alkali soils.

RATE OF PERCOLATION

The results reported in table 2 are averages for the six pots leached. The containers in which the drain waters were collected held approximately 2500 cc. and it was planned to empty, measure, and note the time when the bottles were about two-thirds full. Leaching was continued until an analysis of the drain water indicated that the greater portion of the soluble salts had been leached from the soil.

The water passed rather rapidly through the untreated soil. The first 48 hours yielded an average hourly leaching of 29.4 cc.; during the second period this dropped to 23.6 cc. and then showed a rise. It is quite evident that there is no great increase or decrease in speed of leaching during a period of eighteen days. Probably had this been continued longer there may have been a decrease since the soil tended to compact. The average amount of water leached through the untreated soil was 29.5 cc. per hour. This soil treated with 2 per cent sodium chloride leached at about the same rate at first, but during the second period the leaching dropped to 8.2 cc. per hour and never again throughout the experiment exceeded 11.3 cc. per hour. Therefore the average drainage from the soil treated with sodium chloride was only 11.7 cc. per hour, which is about 40 per cent of that passing through the untreated soil in unit time.

TABLE 2
Rate of percolation in soil treated with various sodium salts

NO TREATMENT		2 PER CENT NaCl		2 PER CENT Na ₂ CO ₃		2 PER CENT Na ₂ SO ₄	
Period	Drainage per hour	Period	Drainage per hour	Period	Drainage per hour	Period	Drainage per hour
hours	cc.	hours	cc.	hours	cc.	hours	cc.
48	29.4	60	26.3	142	8.5	56	36.7
71	23.6	279	8.2	374	5.2	57	32.3
52	36.8	274	8.1	506	3.7	60	30.9
56	36.8	223	11.3	594	2.9	76	28.4
66	28.1	222	8.9	711	2.3	85	22.5
72	25.4	127	7.9	800	1.9	115	17.7
71	26.5			928	1.8	91	19.2
				1096	1.4	83	22.4
				1417	1.1	44	55.2
						29.5	63.9

Soil treated with 2 per cent of sodium carbonate leached very slowly even at first, and by the end of one year only 1 cc. per hour was passing through the soil. The average drainage from this soil was only 3.2 cc. per hour, which is only about 11 per cent of normal as compared with the untreated soil. *The soil and drainage water became dark in color.* It puddled greatly and shrank in volume so that it did not fill the containers. Apparently, the granular structure had been broken down completely (fig. 1).

Soil treated with 2 per cent sodium sulfate leached more rapidly than did the untreated soil. For a short time during the middle of the leaching period this soil for some unknown cause leached more slowly than the untreated soil. However, the average for the entire time was 32.9 cc. per hour which is 112 per cent as compared with the untreated soil. This is due to the flocculating effect of the sodium sulfate upon the soil. It is likely that much of the benefit which has been found (11, 12) to result from the use of sulfates upon this soil is due in a measure to flocculation which increases the aeration of the soil and correspondingly the activity of the aerobic bacteria of the soil.

The average results for the mixture of two sodium salts as compared with the untreated soil are given in table 3.

A soil in which there is a mixture of sodium chloride and sodium sulfate leaches nearly as readily as a soil containing only sodium sulfate. But neither sodium chloride nor sodium sulfate increases the permeability of black alkali soil for water. The soil receiving the mixture of sodium chloride and sodium carbonate leached a little more rapidly at first than soil containing only sodium carbonate. But such soil soon became as impervious to water as soil containing only sodium carbonate. The soil containing the mixture of carbonate and sulfate was in very bad physical condition from the first and leached very slowly. It was impossible to get enough water through the soil to leach out sufficient salt to permit plants to grow.

TABLE 3
Rate of percolation in soil treated with combinations of sodium salts

NO TREATMENT		1 PER CENT NaCl + 1 PER CENT Na ₂ SO ₄		1 PER CENT NaCl + 1 PER CENT Na ₂ CO ₃		1 PER CENT Na ₂ CO ₃ + 1 PER CENT Na ₂ SO ₄	
Period	Drainage per hour	Period	Drainage per hour	Period	Drainage per hour	Period	Drainage per hour
hours	cc.	hours	cc.	hours	cc.	hours	cc.
48	29.4	48	29.2	141	14.7	154	5.5
71	23.6	52	40.6	527	3.2	84	2.2
52	36.8	68	28.3	665	2.1	1135	1.4
56	36.8	45	34.3	812	1.9	966	1.5
56	28.1	87	20.7	1883	1.0	1353	1.3
72	25.4	147	13.7	1328	1.3	1177	1.3
71	26.5	54	34.1				
		48	33.7				
		48	39.9				

The results obtained on leaching a synthetic alkali soil containing a mixture of sodium chloride, sodium sulfate, and sodium carbonate and natural alkali soils are given in table 4. The synthetic soil contained 2 per cent of alkali, one-third of which was chloride, one-third sulfate, and the remaining one-third carbonate. In the Corinne soil the chlorides predominated, in the Richland Acres soil the sulfates, and in the Benson Ward soil, the carbonates.

The prepared soil containing the mixture of chlorides, sulfates, and carbonates leached more slowly than soil containing either chlorides or sulfates, but much more rapidly than soils containing only sodium carbonate.

The natural alkali soils, with the exception of the Corinne soil, leached more rapidly than the prepared soil. The slow leaching of the Corinne soil was due not alone to its alkali content but to the fine texture of the particles composing it. Both the synthetic alkali soil and the Benson Ward soil held very tenaciously to the salts and neither was sufficiently reduced in alkali content to permit the germination of plants even after leaching for 207 and 138 days, respectively. As the salts were removed from the prepared alkali soil the

water passed through more rapidly, but all were in an extremely bad state of tilth after leaching. It is evident from these results that the speed with which water passes through an alkali soil is dependent upon the specific alkalies present and the texture of the soil. This is clearly brought out in table 5

TABLE 4

Rate of percolation in soil treated with chlorides, carbonates and sulfates

NO TREATMENT		NaCl + Na ₂ SO ₄ + Na ₂ CO ₃		CORINNE SOIL		RICHLAND ACRES SOIL		BENSON WARD SOIL	
Period	Drainage per hour	Period	Drainage per hour	Period	Drainage per hour	Period	Drainage per hour	Period	Drainage per hour
hours	cc.	hours	cc.	hours	cc.	hours	cc.	hours	cc.
48	29.4	161	6.6	686	2.6	64	23.5	149	9.0
71	23.6	337	6.1	914	1.9	118	15.2	232	8.0
52	36.8	362	5.5	841	1.8	193	12.2	260	6.9
56	36.8	341	5.6	1212	1.8	216	9.1	192	9.5
66	28.1	416	4.8	1412	1.2	174	7.7	182	11.0
72	25.4	477	4.2			145	8.8	191	10.0
71	26.5	590	4.4					185	10.0
		360	4.7					180	10.9
		277	7.7					189	9.4
		222	7.6					311	7.2
		207	8.9					256	7.4
		212	7.2					271	7.0
		282	8.5					253	7.6
		252	8.5					254	7.2
		270	9.3					223	10.9

TABLE 5

Relative quantities of water passing through each of the various soils in unit time

SOIL	TREATMENT	WATER LEACHED	SOIL	TREATMENT	WATER LEACHED
College	None	100	College	None	100
College	2% Na ₂ SO ₄	112	College	0.66% each NaCl + Na ₂ SO ₄ + Na ₂ CO ₃	23
College	1% NaCl + 1% Na ₂ SO ₄	103			.
Richland Acres		43			
College	2% NaCl	40	College	1% NaCl + 1% Na ₂ CO ₃	14
Benson Ward		30	College	2% Na ₂ CO ₃	11
			College	1% Na ₂ SO ₄ + 1% Na ₂ CO ₃	7
			Corinne		6

which gives the relative quantities of water leached through the soil on the basis of the amount leached through the untreated soil taken as 100.

Sodium sulfate increased the rate of leaching 12 per cent, whereas the mixture of sodium chloride and sodium sulfate increased it 3 per cent. All of the other

treatments greatly decreased the leaching. This was greatest where the carbonate was used and it is evident that the presence of the other salts had little effect in overcoming the puddling effect of the carbonate.

The soils were all leached until an analysis of the drain waters indicated that the greater quantity of the soluble salt which could be removed by water had been carried from the soil. The time required and quantity of water necessary to accomplish this varied greatly with the different soils, as may be seen from table 6.

The time and the quantity of water necessary to remove the salt is a function of the kind of salt in the soil and the texture of the soil. A small volume of water in a short time removed the greater part of the chlorides and sulfates from the soil, but it required a long time to remove the carbonates.

TABLE 6

Leaching necessary to remove the greater portion of the soluble salt from the soil

SOIL	TREATMENT	LENGTH OF PERIOD days	WATER LEACHED liters	SOIL	TREATMENT	LENGTH OF PERIOD days	WATER LEACHED liters
College	None	18	121	College	None	18	121
College	2% NaCl	49	84	College	1% Na ₂ SO ₄ + 1% Na ₂ CO ₃	203	85
College	2% Na ₂ CO ₃	274	140	College	0.66% each NaCl + Na ₂ SO ₄ + Na ₂ CO ₃	199	240
College	2% Na ₂ SO ₄	29	175				
College	1% NaCl + 1% Na ₂ SO ₄	25	153	Corinne		211	79
College	1% NaCl + 1% Na ₂ CO ₃	640		Richland Acres		38	94
				Benson Ward		139	247

RATE OF REMOVAL OF SOLUBLE SALTS

The salts added were determined in each of the fractions of leach water collected. The average results for the sodium salts are given in table 7.

Sodium chloride was rapidly leached from the soil. There was removed in the second period 41 per cent as much salt as during the first period. The quantity per cubic centimeter was, however, 47 per cent greater during the second period than during the first. This undoubtedly occurred because the soil held the water longer, which permitted it to become more nearly saturated with salt before it drained from the soil. The yield in the third was only 2 per cent per hour of that of the first and by the fourth period it had been reduced to a fraction of 1 per cent. The quantity of salt per cubic centimeter by the fourth period had been reduced to 0.2 mgm. per cubic centimeter which indicated that most of the salt soluble in water had been leached from the soil.

Less sodium carbonate was leached from the soil per hour during the first period than sodium chloride. The quantity per cubic centimeter, however,

was much greater. By the fifth period the quantity being removed had become nearly constant, with each cubic centimeter of water carrying 2 mgm. of sodium carbonate. It would appear that uncombined or unadsorbed sodium carbonate is readily removed by water, but the combined or adsorbed salt is removed with great difficulty.

Sodium sulfate was leached from the soil even more readily than sodium chloride. These results would indicate that no trouble should be experienced in leaching sodium chloride or sulfate from a soil such as this. This should not, however, be taken as the case with all soils, for the texture of this soil was fairly coarse and it was well supplied with calcium and magnesium carbonate (5). There was no indication from the texture or color of the soil or analysis of the drainage water that the sodium chloride was being transformed into the carbonate. The removal of sodium carbonate from this soil presents considerable difficulty, for even after it had been leached for 274 days and

TABLE 7

Rate of removal of NaCl, Na₂CO₃ and Na₂SO₄ from soil containing 2 per cent of these same salts

NaCl REMOVED			Na ₂ CO ₃ REMOVED			Na ₂ SO ₄ REMOVED		
Period	Per hour	Per cubic centimeter	Period	Per hour	Per cubic centimeter	Period	Per hour	Per cubic centimeter
hours	mgm.	mgm.	hours	mgm.	mgm.	hours	mgm.	mgm.
60	712.0	27.1	142	438.1	51.5	56	1471.0	40.1
279	291.3	24.2	374	98.5	18.9	57	787.5	24.4
274	12.0	1.4	506	18.2	4.9	60	339.9	11.0
223	0.1	0.08	594	7.3	2.5	76	100.4	3.5
			711	4.7	2.0	85	37.4	1.7
			800	2.8	1.5	115	9.2	0.5
			928	2.6	1.4	91	3.1	0.2
			1096	2.2	1.6	83	1.5	0.07

140 liters of water had passed through it the soil contained sufficient black alkali to prevent the growth of plants. In addition to the large quantities of sodium carbonate present several other factors were not ideal for plant growth after leaching as will be pointed out in this and later papers.

It is evident from table 8 that in a mixture of sodium chloride and sodium sulfate the chloride leaches from the soil more readily than the sulfate. By the end of 168 hours the drainage water was nearly free from sodium chloride but was carrying appreciable quantities of sodium sulfate at the end of 501 hours of leaching. The sulfate is adsorbed more firmly by the soil in mixtures and as individual salts than the chloride. Soil containing sodium chloride and sodium carbonate yields its chloride readily but the carbonate is tenaciously held. Even after being leached for 640 days soil still yielded considerable sodium carbonate. Moreover, it is evident from these results that sodium carbonate retards the leaching of sodium chloride from the soil. This is also true for sodium sulfate. However, it does appear that the carbonate

leaches out more readily in the presence of sodium sulfate than in the presence of sodium chloride, which is due to the flocculating action of the sulfate.

TABLE 8

Rate of removal of sodium salts from soil containing combinations of the following salts

1 PER CENT NaCl + 1 PER CENT NaSO ₄			1 PER CENT NaCl + 1 PER CENT Na ₂ CO ₃			1 PER CENT Na ₂ CO ₃ + 1 PER CENT NaSO ₄		
Period	NaCl removed per hour	NaSO ₄ removed per hour	Period	NaCl removed per hour	Na ₂ CO ₃ removed per hour	Period	Na ₂ CO ₃ removed per hour	NaSO ₄ removed per hour
hours	mgm.	mgm.	hours	mgm.	mgm.	hours	mgm.	mgm.
48	940.2	478.7	141	454.6	14.0	154	14.1	293.4
52	746.1	637.1	527	39.9	11.8	843	8.8	41.4
68	26.1	321.1	665	2.3	10.3	1135	5.5	2.0
45	1.0	130.3	812		5.3	966	4.5	0.08
87		16.2	1883		2.0			
147		2.1	1328					
54		4.5						
48		3.5						

TABLE 9

Rate of removal of sodium salts from synthetic and natural alkali soils

SYNTHETIC ALKALI SOIL			CORINNE SOIL			RICHLAND ACRES SOIL			BENSON WARD SOIL						
Period	Removed per hour			Period	Removed per hour			Period	Removed per hour			Period	Removed per hour		
	NaCl	NaSO ₄	Na ₂ CO ₃		NaCl	NaSO ₄	Na ₂ CO ₃		NaCl	NaSO ₄	Na ₂ CO ₃		NaCl	NaSO ₄	Na ₂ CO ₃
hours	mgm.	mgm.	mgm.	hours	mgm.	mgm.	mgm.	hours	mgm.	mgm.	mgm.	hours	mgm.	mgm.	mgm.
161	272.4	265.0	5.4	658	502.8	8.1	64	163.4	727.3	149	605.1	386.6	244.3		
337	30.5	44.8	13.8	914	34.3	0.8	118	18.7	168.0	232	24.7	73.2	11.4		
362	1.4	1.3	10.6	841	2.4	0.05	193		4.9	260	3.8	30.6	3.0		
341	0.1	0.4	9.2	1212	0.5		216		0.9	192	0.9	20.0	1.7		
416		0.2	6.4	1412			174		0.5	182		15.7	1.2		
477		0.2	4.0				145		0.5	191		12.2	0.8		
590			2.3							185			9.5		
360			3.5							180			9.4		
277			4.1							189			7.5		
222			4.6							311			4.3		
207			4.3							256			4.9		
212			4.8							271			4.4		
282			2.9							253			4.2		
252			2.1							254			3.8		
270			1.3							223			3.7		

The average results for a soil containing mixtures of sodium chloride, sodium carbonate, and sodium sulfate and for natural alkali soils are given in table 9. These soils were similar in the order in which they parted with their soluble

salts. The first washings carried away most of the chloride and sulfate. Often the first water leached through the soil was nearly saturated with salt. The carbonate, both in the natural alkali soil and the synthetic soil, was rapidly leached from the soil during the first period, but later it was only slowly removed. The slow leaching of sodium carbonate from the soil was due to two factors, viz., (a) the extremely bad physical condition of the soil and (b) the chemical combination or adsorption of the black alkali by the various colloidal constituents of the soil. The second factor was of the greater importance, for table 4 shows that although the black alkali soil leached extremely slowly as compared with the white, yet the speed of leaching did not decrease after long periods of leaching. The quantity of sodium carbonate, which the drainage water was carrying from the soil, was very small even though the soil still contained great quantities of sodium carbonate, as may be seen from table 10.

TABLE 10
Recovery of salts from prepared and natural alkali soils

SOIL	TREATMENT			NaCl RECOVERED		Na ₂ SO ₄ RECOVERED		Na ₂ CO ₃ RECOVERED	
	NaCl	Na ₂ SO ₄	Na ₂ CO ₃	gm	per cent	gm	per cent	gm	per cent
	180	180	180	128.9	71.6	159.9	88.8	120.5	66.9
College . . .	180	180	180					22.0	24.5
	90	90	90	85.0	94.5	86.0	95.6		
	90	90	90	85.0	94.5	83.0	92.2	19.4	21.6
	60	60	60	54.8	91.3	58.6	97.7	26.0	43.3
				379.1		6.3			
Corinne . . .				12.7		67.8			
Richland Acres . . .				97.0		40.6		103.7	
Benson Ward . . .									

Eighty-four liters of water passed through the soil containing 2 per cent of sodium chloride in 49 days and removed 71.6 per cent of the sodium chloride from the soil. One hundred and seventy-five liters leached through the soil treated with 2 per cent sodium sulfate in 29 days and removed 88.8 per cent of the sulfate from the soil, whereas only 140 liters of water drained through the soil treated with carbonate in 274 days and removed 66.9 per cent of the sodium carbonate from the soil.

It is evident from these results that the speed with which the water passes through the soil and the ease with which the salts are removed is a function of the kind and the quantity of salt within the soil. It is greatest in the sulfate and least in the carbonate.

A mixture of sodium chloride and sodium carbonate leached more slowly than either of the salts separately. In 640 days only 93 liters of water passed through soil treated with these two salts and removed 24.5 per cent and 94.5 per cent, respectively. Sodium sulfate in every case accelerated the

speed with which water passed through the soil and also the rate with which the chloride was removed. But even in the presence of sulfate, sodium carbonate was leached from the soil extremely slowly. During the leaching 88.8-97.7 per cent of the sulfate was removed from the soil, 71.6-94.5 per cent of the sodium chloride, and only 21.6-66.9 per cent of the sodium carbonate. It is evident from the results as a whole that the prepared alkali soil containing sodium chloride, sodium sulfate, and sodium carbonate reacts very similarly to the natural alkali soil. In each case the carbonate was the substance giving the difficulty, as was the case in each of the natural soils tested.

CALCIUM AND MAGNESIUM CONTENT OF LEACH WATER

All four soils were high in calcium and magnesium. The College Farm soil, which is normally free from alkali and which has been used in all of this work for the preparation of the prepared alkali soil, contained 33.31 per cent of acid soluble material. It contains 7.41 per cent of calcium oxide and 4.15 per cent of magnesium oxide. This is a calcium-magnesium ratio of 7:4 which is the ratio Loew and May (13) found to be best for the germination and growth of cereals. They were, however, dealing with soluble calcium and magnesium, whereas this is mainly in the insoluble form, much of it probably being in the form of the double salt $\text{CaMg}(\text{CO}_3)_2$. The question naturally arises as to the order in which these two bases are dissolved out by water both in the absence and presence of the various alkali salts. To answer this, all of the drainage waters were analyzed for calcium and magnesium. The average results for the variously treated soils are given in table 11. The drainage water was analyzed when approximately 2000 cc. had leached from the soil.

A number of very interesting features appear in these results. For instance, the calcium magnesium ratio for salts leached from untreated soil is narrow, averaging 1.2-1.0 which is ideal according to the findings of Furuta (6), Aso (1, 2), Bernardini and Corso (3), and Bernardini and Siniscalchi (4) for wheat, rye, oats, and other plants with small leaf surface. The constant leaching of these soils by water, judging from the order in which the lime and magnesia are being carried out, should never leave them toxic because of a wrong lime-magnesia ratio.

On the other hand, the soil which was treated with 2 per cent sodium chloride yielded large quantities of calcium in the early leach water, probably because of the formation of calcium chloride and sodium carbonate. This gave a very wide lime to magnesia ratio, which was as wide as 7.1 to 1 in some of the drainage waters. As the soluble salts were washed from the soil the ratio became narrow and toward the last was as low as 1 to 3, which according to Loew and his coworkers (13) would cause a very unproductive nutritive medium for the growth of plants. It would therefore seem that the long unproductive period following the drainage of alkali soil is due at times to a toxic lime-magnesia ratio of the soil solution and should be rectified by the addition of lime to the soil. The lime would not only cause a better state

TABLE 11

Calcium oxide, magnesium oxide, and lime magnesia ratio in drainage from treated soils and natural alkali soils

LEACH- ING	NO SALT			2 PER CENT NaCl			2 PER CENT Na ₂ SO ₄			2 PER CENT Na ₂ CO ₃			1 PER CENT NaCl + 1 PER CENT Na ₂ SO ₄			1 PER CENT NaCl + 1 PER CENT Na ₂ CO ₃		
	CaO	MgO	CaO/MgO	CaO	MgO	CaO/MgO	CaO	MgO	CaO/MgO	CaO	MgO	CaO/MgO	CaO	MgO	CaO/MgO	CaO	MgO	CaO/MgO
	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.
1	4.6	3.0	1.5	60.4	19.9	3.1	13.5	15.1	0.9	2.0	0.82	2.5	18.5	12.6	1.5	2.1	1.8	1.2
2	1.2	1.5	0.8	56.4	17.4	3.2	11.1	6.8	1.6	2.5	0.83	3.1	18.6	12.9	1.4	2.4	1.7	1.4
3	0.7	1.5	0.5	31.1	4.1	7.1	7.2	2.3	3.1	1.7	0.44	2	8.9	3.5	2.5	2.3	1.3	1.8
4	2.1	1.0	2.1	1.4	2.9	0.5	3.9	1.0	3.9	1.5	0.27	5	3.1	1.5	2.1	1.4	0.6	2.3
5	0.5	0.5	1.0	0.8	2.3	0.3	2.6	0.6	4.3	1.2	0.34	0	2.0	0.8	2.5	1.2	1.0	1.2
6	0.6	0.4	1.5	0.5	1.5	0.3	1.9	0.44	8	1.2	1.2	6.0	1.4	0.5	2.8	1.2	0.5	2.4
7							2.2	1.3	1.7	0.8	0.24	0	1.2	0	52.4			
8							1.4	0.34	7	0.9	0.24	5	0.8	0	51.6			
9							1.3	0.7	2.0									
10							1.3	0.5	2.6									
11																		
12																		
13																		
Total....	9.2	7.9	1.2	150.6	48.1	3.2	46.4	29.0	1.6	11.8	3.1	3.8	54.5	32.8	1.7	10.6	6.9	1.5

TABLE 11—Continued

LEACH- ING	1 PER CENT Na ₂ SO ₄ + 1 PER CENT Na ₂ CO ₃			0.66 PER CENT EACH NaCl, Na ₂ SO ₄ , Na ₂ CO ₃			CORINNE SOIL			RICHLAND ACRES SOIL			BENSON WARD SOIL		
	CaO	MgO	CaO/MgO	CaO	MgO	CaO/MgO	CaO	MgO	CaO/MgO	CaO	MgO	CaO/MgO	CaO	MgO	CaO/MgO
	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.	gm.
1	2.5	2.0	2.3	9.9	6.8	1.5	26.3	73.2	0.3	14.6	65.0	0.2	0.6	0.4	1.5
2	3.6	2.4	1.5	6.0	2.5	2.4	2.6	6.0	0.4	1.5	17.6	0.1	6.7	0.6	11.1
3	3.3	0.9	3.7	2.1	0.7	3.0	1.2	9.8	0.1	1.2	1.2	1.0	2.9	0.5	5.8
4	1.0	0.5	2.0	1.1	0.5	2.2	1.1	0.6	1.9	0.8	1.0	0.8	1.1	0.5	2.2
5	1.7	0.6	2.8	1.1	0.6	1.8	2.0	1.1	1.9	0.5	1.1	0.5	0.8	0.5	1.6
6	1.1	0.5	2.2	1.0	0.4	2.5				0.6	0.5	1.2	1.1	0.5	2.2
7				1.0	0.3	3.3							0.7	0.3	2.3
8				1.0	0.6	1.8							0.6	0.2	3.0
9				0.9	0.3	3.0							0.7	0.3	2.3
10				0.7	0.2	3.5							0.6	0.1	6.0
11				1.0	0.3	3.3							0.5	0.2	2.5
12				1.0	0.5	2.0									
13				1.9	0.6	3.1									
Total....	13.2	6.9	1.9	28.7	14.3	2.0	33.2	24.7	1.3	19.2	86.4	0.2	17.0	4.4	3.9

of tilth but also a proper lime-magnesia ratio. The rapid removal of the calcium as opposed to the magnesium from the soil may also yield a soil deficient in total calcium as compared to total magnesium. It is quite conceivable that this may occasionally occur when chlorides are used over long periods in commercial fertilizers.

Soil containing 2 per cent of sodium sulfate yielded more calcium and magnesium in the leach water than did untreated soil, but only 30 and 60 per cent, respectively, as much as was yielded by soil treated with sodium chloride. The lime-magnesia ratio was narrow in the first leaching and wider later. However, the average ratio for the entire leaching was 1.6 to 1, and it never became narrow enough to indicate a toxic condition. Moreover, the speed with which the two salts were carried from the soil was such that the ratio in the soil would not be upset enough to render it toxic. Hence, viewed in the light of these results fertilizers containing sulfates would probably be safer in long continued experiments on this soil than would fertilizers containing chlorides.

Less magnesium and only slightly greater quantities of calcium were leached from soil treated with sodium carbonate than from untreated soil. There was a wide calcium-magnesium ratio throughout the leaching process and no indication that the toxic ratio would be reached in soil containing black alkali. It is significant that thirteen times as much calcium and fifteen times as much magnesium was carried away in drain water where sodium chloride was the alkali present as where sodium carbonate was the salt present.

Soil containing a mixture of sodium chloride and sodium sulfate lost more calcium and magnesium than soil containing only sodium sulfate and considerably less than the same soil containing only sodium chloride. The lime-magnesia ratio was 1.7 to 1 which does not indicate toxicity as is the case in the last leaching from soil treated with sodium chloride.

Soil containing mixtures of sodium chloride and sodium carbonate and of sodium sulfate and sodium carbonate parted with their calcium slowly and as an average lost no more than the untreated soil. In every case the quantity of calcium exceeded the quantity of magnesium and usually with a margin great enough to render the solution non-toxic according to Loew's lime-magnesia theory.

Because of the extremely long time necessary to leach the soil containing the three salts, this series lost more calcium and magnesium than did the untreated soil or those soils containing only a single salt. The excess loss of calcium over that of magnesium was most noticeable here.

The quantity of calcium lost from the Corinne soil was about the same as that leached from the prepared alkali soil. However, the magnesium lost from the Corinne soil was much greater and the quantity of magnesium in the leachings greatly exceeded the quantity of lime. This was due to the large quantities of soluble magnesium chloride and sulfate in the original soil and it cannot be assumed that magnesium carbonate was rendered soluble. This

was true in both the Corinne and Richland Acres soil from which a great excess of magnesium over calcium left the soil in the first drain waters. In the Benson Ward soil the lime-magnesia ratio was wide throughout with only small quantities of the salts leached from the soil.

PHOSPHORUS CONTENT OF DRAINAGE WATERS

The drainage waters from each pot were analyzed for phosphorus and the average results are given in table 12. Analyses were made on each bottle which contained approximately 2000 cc. of the leach water. This fractional analysis gives the order in which the phosphorus left the soil. It is interesting to note that not only while the large quantities of alkali were leaving the soil

TABLE 12
Phosphorus leached from synthetic and natural alkali soils

LEACHING	2 PER CENT NaCl		2 PER CENT Na ₂ SO ₄		2 PER CENT Na ₂ O ₂		1 PER CENT NaCl + 1 PER CENT Na ₂ SO ₄		1 PER CENT NaCl + 1 PER CENT Na ₂ CO ₃		1 PER CENT Na ₂ SO ₄ + 1 PER CENT Na ₂ CO ₃		0.66 PER CENT EACH NaCl Na ₂ SO ₄ Na ₂ CO ₃	CORINNE SOIL	RICH-LAND ACRES SOIL	BENSON WARD SOIL
	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
1	3.81	3.49	18.30	323.20	7.70	15.28	20.61	7.05	8.18	1.89	805.98					
2	4.48	6.68	18.86	139.00	11.16	38.70	37.95	25.11	12.73	5.50	144.00					
3	5.06	26.43	10.16	54.20	12.91	37.89	28.46	24.86	16.86	2.95	69.46					
4	6.48	35.18	8.69	34.39	10.27	28.54	19.44	23.77	22.49	3.14	35.16					
5	4.35	34.50	13.97	28.49	16.36	27.16	22.20	23.18	19.54	1.76	22.75					
6	4.65	20.81	11.12	26.07	18.67	27.93	21.65	22.74			19.40					
7			8.42	25.16	19.40			22.24			13.79					
8			5.87	21.02	15.32			20.24			11.16					
9			6.85	19.02	21.26			21.50			9.85					
10					14.99			20.25			9.60					
11								18.90			7.70					
12								17.42			6.42					
13								17.88								
Total....	28.83	127.09	102.24	670.54	148.04	175.50	150.31	265.14	79.80	15.24	1155.27					

but even toward the end of the leaching period large quantities of phosphorus were leaving in the drainage water.

One may conclude from these results that the long unproductive period following the leaching of alkali soil cannot be due to the lack of available phosphorus, for the alkali soils are yielding one to five times as much water-soluble phosphorus as are productive soils. It is, however, the more easily available phosphorus which is being taken from the soil and it is quite possible that after considerable leaching and the removal of the greater part of the soluble salt the water-soluble phosphorus may be very low. Moreover, the bacterial activities which tend to render it soluble are low. Hence, for a time after leaching alkali soil may be low in easily available phosphorus.

The carbonate liberated the largest quantities of phosphorus, the chloride less, and the sulfate least. Even the sulfate liberated appreciable quantities. If we consider the removed phosphorus from the untreated soil as 100, the amount removed from soil treated with sodium sulfate is 355; with sodium chloride, 441; with sodium carbonate, 2325; with sodium chloride and sodium sulfate, 514; with sodium sulfate and sodium carbonate, 521; with sodium chloride and sodium carbonate, 609; and with the mixture of the three salts, 92. The Benson Ward soil yielded considerably more phosphorus than any of the synthetic alkali soils. The other two natural alkali soils yielded smaller quantities of phosphorus. This substantiates the theory which was argued at some length by the senior author elsewhere (10)—that the beneficial action of some common soil amendments is due largely to their solvent action on insoluble plant-food and that this is especially marked in the case of the phosphorus. Crops grown on soil treated with chlorides and sulfates often yield more heavily and the phosphorus content of the plant is usually greater than where the chloride or sulfate is not added to the soil. Wherever soil is deficient in available phosphorus this should occur; hence, it accounts for the common phenomenon of no increase where chlorides or sulfates are added to soil already supplied with available phosphorus. Moreover, these salts often exert another effect, that of increased bacterial activity which increases available nitrogen since it has been shown that these salts increase ammonification (8), nitrification (11), and azofication (12). It is often hard to show that there is an increase of water-soluble phosphorus in soil treated with soluble salts (7). This, as has been shown elsewhere (10), is often due to rapid metabolism of phosphorus by the microflora of the soil by which it is changed to insoluble organic compounds. This would not, however, have occurred in this soil since the bacterial activities of the soil have been shown to be very materially reduced by these concentrations of salts (9). Therefore, the effect which is noted here is due to the direct solvent action of the soil solution upon the inorganic phosphates and to the action of sodium carbonate upon the organic phosphorus of the soil. However, when the concentration of salt is low its stimulating influence upon the microflora would result in increased acids which would have an appreciable influence on the soluble plant-food of the soil.

POTASSIUM CONTENT OF DRAINAGE WATERS

Total potassium determinations were made on each fraction of the drainage water and the average results are given in table 13. The early leachings from all the prepared and natural alkali soils were very rich in potassium as compared with non-alkali soil. Of the soils treated with only one salt the greatest quantities of potassium were rendered soluble by the chloride, less by the sulfate, and least by the carbonate. It is evident that soil such as this would respond greatly to soil amendments which would render available large quantities of potassium. The mixtures of the salts in all cases were more

effective than the single salt. In all of the natural alkali soils large quantities of potassium were found in the leachings at first, but it is significant that as leaching continued in all the soils the quantity of potassium in the drainage water very materially decreased. In some cases very small quantities were being removed in the leach waters. These results point strongly to the conclusion that the unproductive period following the leaching of alkali soil is due, in a measure, to a lack of available potassium. The addition of organic matter to such a soil not only causes better tilth but increases bacterial activity, and the increased bacterial activity should result in more available potassium. The excess losses of soluble potassium from these alkali soils must have been due to a direct solvent action of the salt and not to increased bacterial action.

TABLE 13
Potassium leached from synthetic and natural alkali soils

LEACHING	SOIL	2 PER	1 PER	1 PER	0.66 PER	CORNINNE	RICH-	BENSON			
		CENT NaCl	CENT Na ₂ SO ₄	CENT Na ₂ CO ₃	CENT Na ₂ SO ₄		LAND ACRES SOIL		WARD SOIL		
		mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.	mgm.
1	65.4	259.2	137.9	114.9	269.4	183.8	132.2	270.9	1965.0	535.0	266.4
2	37.9	254.8	68.8	64.6	364.3	103.8	153.0	162.2	538.0	253.6	155.8
3	44.7	17.4	69.5	41.3	80.6	83.9	112.0	59.1	144.6	117.5	99.6
4	36.1	15.1	35.7	18.3	54.3	52.5	60.3	61.9	117.8	158.2	82.3
5	31.8	13.8	28.7	13.1	44.7	55.4	64.6	57.3	90.1	71.6	57.6
6	30.5	2.0	20.7	17.5	36.6	53.5	62.8	60.2		55.8	48.1
7			38.1	37.2	16.1			35.8			45.3
8			14.7	26.4	28.7			31.0			39.7
9			10.6	21.7	36.1			23.9			37.1
10								16.1			38.1
11								18.4			29.3
12								20.5			29.3
13								1.5			
Total....	246.4	563.0	423.8	355.0	930.8	532.9	584.9	818.8	2855.5	1191.7	928.6

NITROGEN CONTENT OF LEACHINGS

Determinations for nitrogen were made on composite samples of the leach water. The results given in table 14 correspond to the totals given in previous tables.

In every case the salt-treated soil lost more nitrogen than the untreated soil. The sulfate-treated soil yielded nearly twice as much, the chloride-treated nearly five times, and the carbonate-treated soil nine times as much as the untreated soil. Most of the nitrogen was in the form of organic material and the weak salt solution, which was a good protein solvent, carried out large quantities. It is significant that the chloride and especially the carbonate, both of which are hard to leach from the soil and leave it in a very bad state of

tilth, carried out the greater quantity of organic nitrogen. The natural alkali soils, except for the Benson Ward soil which contained large quantities of nitrates, yielded less nitrogen than most of the synthetic alkali soils. There is no relationship between the phosphorus and nitrogen of the soil except where sodium carbonate was applied to the soil. This indicates that it is the inorganic phosphates which are being rendered soluble and carried from the soil by the salts and not the phosphoproteins and nucleoproteins, as was the case with sodium carbonate. The phosphorus-nitrogen ratio varied from 1 to 1.3 in the case of soil treated with sodium chloride and sodium sulfate to 1 to 7.2 in the soil treated with sodium carbonate and sodium sulfate.

TABLE 14
Nitrogen leached from synthetic and natural soils

SOIL	TREATMENT	NITROGEN IN TOTAL LEACH WATER
		mgm.
College	Untreated	119.8
	2% NaCl	558.1
	2% Na ₂ SO ₄	279.3
	2% Na ₂ CO ₃	2666.2
	1% NaCl + 1% Na ₂ SO ₄	498.1
	1% NaCl + 1% Na ₂ CO ₃	948.1
	1% Na ₂ CO ₃ + 1% Na ₂ SO ₄	1096.2
	0.66% each NaCl, Na ₂ SO ₄ , Na ₂ CO ₃	673.6
Corinne		334.2
Richland Acres		225.0
Benson Ward		1267.7

ORGANIC CARBON CONTENT OF LEACHINGS

The carbon content of the drainage waters was determined by the chromate methods (15). Considerable difficulty was experienced in obtaining concordant duplicates and the results obtained were not very satisfactory. Table 15 shows that the organic carbon content of the untreated soil was quite constant in each fraction of the leach water, but in all the salt-treated soil the first drainage water was much richer in carbon than later fractions. The salts apparently rendered it soluble so it readily leached from the soil and left the soil almost devoid of organic matter. Soil treated with sulfate lost no more organic carbon than the untreated soil, whereas soil treated with chloride and carbonate lost large quantities of organic matter.

The carbon-nitrogen ratio was wide in the leachings of the untreated soil and narrow in the alkali soil which indicates that the organic material carried away in the drainage water was proteinaceous. The black alkali soil yielded a drainage water which was very rich in nitrogen as compared with its carbon. It probably lost most of its readily ammonifying material and retained carbonaceous material which would be attacked only slowly by the microflora of the soil.

RELATIVE AMOUNTS OF PLANT NUTRIENTS LOST BY LEACHING

That the drainage water of the prepared alkali soil was rich in valuable plant nutrients is brought out in table 16 in which the losses from the untreated soil are taken as 100.

In three of the salt treatments less magnesia was extracted than in the untreated soil, and in one case less carbon was extracted where salt was present.

TABLE 15

Carbon content and carbon-nitrogen ratio of leachings from synthetic and natural alkali soils

SOIL	TREATMENT	CARBON IN LEACHINGS	CARBON- NITROGEN RATIO IN LEACHINGS
			mgm.
College	Untreated	2566	21.4:1
	2% NaCl	5131	9.1:1
	2% Na ₂ SO ₄	2439	8.7:1
	2% Na ₂ CO ₃	9414	3.5:1
	1% NaCl + 1% Na ₂ SO ₄	6703	13.4:1
	1% NaCl + 1% Na ₂ CO ₃	9176	9.7:1
	1% Na ₂ SO ₄ + 1% Na ₂ CO ₃	9591	8.8:1
	0.66% each NaCl, Na ₂ SO ₄ , Na ₂ CO ₃	11607	17.2:1
Corinne		762	2.3:1
Richland Acres		1777	7.9:1
Benson Ward		16408	13.0:1

TABLE 16

Plant nutrients in leachings from synthetic alkali soil

ELEMENT	UN-TREATED SOIL	SOIL + 2 PER CENT NaCl	SOIL + 2 PER CENT Na ₂ SO ₄	SOIL + 2 PER CENT Na ₂ CO ₃	SOIL + 1 PER CENT EACH NaCl Na ₂ SO ₄	SOIL + 1 PER CENT EACH NaCl Na ₂ CO ₃	SOIL + 1 PER CENT EACH Na ₂ SO ₄ , Na ₂ CO ₃	
Calcium.....	100	1637	504	128	592	115	143	312
Magnesium.....	100	609	367	39	415	87	87	155
Phosphorus.....	100	441	355	2325	514	609	521	920
Potassium.....	100	229	172	144	378	216	237	332
Nitrogen.....	100	466	233	223	416	791	910	562
Carbon.....	100	200	95	367	261	358	374	452

In all other cases the salt increased the solubility of the tested constituent. Twenty-three times as much phosphorus was extracted from soil treated with 2 per cent of sodium carbonate as was lost from the check. Although most of this phosphorus came from the insoluble phosphates, yet the large quantities of carbon, nitrogen, and phosphorus extracted in the presence of sodium carbonate makes it appear certain that in this treatment much of the organic phosphorus is being carried from the soil in the drainage waters.

SUMMARY

The soils used in this work were three natural alkali soils: one in which the chlorides predominated, a second in which the sulfates predominated, and a third which was heavily charged with sodium carbonate. A productive calcareous silt loam was also used. This was made into an alkali soil by various treatments with sodium chloride, sulfate, and carbonate.

These were leached in 2-gallon jars until the greater portions of the salts were removed. The amount of leaching required is given in table 6.

The natural alkali soil behaved similarly to the non-alkali soil treated with a mixture of the salts. Soil treated with sodium carbonate leached very slowly and after leaching was in very bad tilth. The soil treated with sodium chloride leached more readily than the sodium carbonate soil but was slow as compared with the natural soil and remained in a bad physical condition. The soil treated with sodium sulfate leached rapidly and was left in fair tilth.

Sodium sulfate leached readily from the soil and the first drainage water was nearly saturated; 88.8-97.7 per cent of the sulfate was leached from the soil. The first water passing through the soil treated with sodium chloride was heavily charged with chloride and 71.6-94.5 per cent of the chloride was recovered in the drainage water. Soil treated with sodium carbonate leached very slowly; toward the end in one case the rate per hour was one cubic centimeter containing only 0.07 mgm. of sodium carbonate. From 21.6 to 66.9 per cent of the added carbonate was recovered in the leach water. It was therefore impossible by the leaching process to free a column of soil one foot in depth and provided with ideal underdrainage from sodium carbonate to such an extent that crops would grow upon it. This was due to two factors: (a) Sodium carbonate breaks down the structure of a fine-grained soil to such an extent that it is rendered almost impervious to water; (b) the sodium carbonate is held so firmly by the colloidal material that it cannot be washed out by water.

From 1.2 to 16.4 times as much lime was leached from alkali soil as from normal soil which shows that the various salts greatly increased the solubility of calcium. This effect was least in the case of sodium carbonate and greatest in the case of sodium chloride. From 0.4 to 6 times as much magnesium was leached from treated soil as from untreated soil. The order of solubility is the same as that of lime. The order with which the two ions, calcium and magnesium, leave the soil make it possible for some soils to be left after leaching with a toxic lime-magnesium ratio and it is probable that at times the addition of lime to a drained alkali field benefits the soil in two ways, (a) by improving the tilth due to the flocculant action of the lime and (b) by causing a productive lime-magnesia ratio.

From 3.6 to 23.3 times as much phosphorus was leached from the treated soil as from the untreated soil. This excess was greatest when sodium carbonate was added to the soil and least when sodium sulfate was applied. Most of

it was due to the direct action of the salt on the insoluble inorganic phosphorus of the soil. However, a study of the carbon-nitrogen-phosphorus content of the drainage waters from soil treated with sodium-carbonate indicated that considerable quantities of organic phosphorus were carried out in the drainage waters of the soil treated with sodium carbonate.

The potassium content of the treated soil was 1.5-3.8 times as great as that of the untreated soil. The greatest quantity was found in the leachings from soil treated with sodium chloride and least in soil treated with sodium carbonate.

The nitrogen content of the treated soil after leaching was 2.2 to 9.1 times that of the untreated soil and the carbon content, 1 to 4.5 times. This difference in losses shows that proteinaceous material was rendered soluble.

The results substantiate the theory argued by the senior author in a former paper—that soil amendments often make more plant-food soluble, especially phosphorus and nitrogen.

The results make it appear likely that the long unproductive period following the drainage of alkali soil is caused by (a) the leaching of much of the readily available plant-food which makes necessary a period of weathering before sufficient plant-food is available for crop production, (b) the poor state of tilth of the drained soil and sometimes (c) a toxic lime-magnesia ratio.

REFERENCES

- (1) Aso, K. 1902 On the influence of different ratios of lime and magnesia upon the development of plants. *In* Bul. Col. Agr. Imp. Tokyo, v. 4, no. 5, p. 361-370.
- (2) Aso, K. 1904 On the influence of different ratios of lime to magnesia to the growth of rice. *In* Jour. Col. Agr. Tokyo, Japan, v. 6, p. 97-102.
- (3) BERNARDINI, L., AND CORSO, G. 1907 The influence of varying proportions of calcium and magnesium on the development of plants. *In* Ann. Rpt. Scuola Sup. Agr., partici 2, ser. 7, p. 16; *abs. in* Exp. Sta. Rec., v. 21, p. 30.
- (4) BERNARDINI, L., AND SINISCALCHI, A. 1908 Concerning the influence of various relations between lime and magnesia on the development of plants, II. *In* Ann. Rpt. Scuola Sup. Agr., portici 2, ser. 8, p. 19; *abs. in* Exp. Sta. Rec., v. 22, p. 433.
- (5) CUMMINS, A. B. 1921 Formation of black alkali in soils. *In* Calif. Agr. Exp. Sta. Ann. Rpt. 1920-1921, p. 24.
- (6) FURUTA, T. 1902 To what extent should soil be limed? *In* Bul. Col. Agr. Tokyo, Japan, v. 4, p. 371-379.
- (7) GREAVES, J. E. 1910 Effects of soluble salts on insoluble phosphates. *In* Jour. Biol. Chem., v. 7, p. 287-319.
- (8) GREAVES, J. E. 1916 The influence of salts on the bacterial activities of the soil. *In* Soil Sci., v. 2, p. 443-480.
- (9) GREAVES, J. E. 1922 Influence of salts on bacterial activities of the soil. *In* Bot. Gaz., v. 73, no. 3, p. 161-180.
- (10) GREAVES, J. E., AND CARTER, E. G. 1919 The action of some common soil amendments. *In* Soil Sci., v. 7, p. 121-160.
- (11) GREAVES, J. E., CARTER, E. G., AND GOLDFORPE, H. C. 1919 Influence of salts on the nitric nitrogen accumulation of the soil. *In* Jour. Agr. Res., v. 16, p. 107-135.
- (12) GREAVES, J. E., CARTER, E. G., AND LUND, YEPFA 1922 Influence of soluble salts on azofication in soil. *In* Soil Sci., v. 13, p. 481-499.

- (13) LOEW, OSCAR, AND MAY, D. W. 1901 The relation of lime and magnesia to plant growth. U. S. Dept. Agr. Bur. Plant Indus., Bul 1.
- (14) SUZUKI, S. 1905 On the injurious effect of an excess of lime applied to the soil. *In* Bul. Col. Agr., Tokyo, Japan, v. 6, p. 347-351.
- (15) WAYNICK, D. J. 1919 A simplified wet combustion method for the determination of carbon in soil. *In* Jour. Indus. Engin. Chem., v. 11, no. 7, p. 634-637.
- (16) YODER, P. A. 1904 A new centrifugal soil clutriator. Utah Agr. Exp. Sta. Bul. 80.

THE EFFECT OF PLANTS ON THE CONCENTRATION OF DRAINAGE WATER FROM THE CORNELL LYSIMETERS

BENJAMIN D. WILSON

Cornell University

Received for publication September 20, 1923

A slight change in the method of handling the aliquot samples of drainage water from the Cornell lysimeters has resulted in the analysis of the percolates for total solids at various times during the year. It is the purpose of this paper to present the concentration of the leachings from certain of the planted and unplanted lysimeters, over a period of three years. The results from eight of these will suffice to show the effect that plants have had on the concentration of the percolated water from two distinct types of soil.

Since the lysimeters and the soils with which they are filled have been fully described by Lyon and Bizzell (1, 2), it will not be necessary to repeat their descriptions here.

Six of the eight lysimeters selected were filled with Dunkirk clay loam soil in 1909. Two of these have been kept free of vegetation, two in grass continuously, and two have been planted to a five-year rotation of maize, oats and wheat followed by two years of hay. One of each of these three pairs of tanks has received an application of burnt lime at the beginning of each rotation and all of them have received farm manure. Results from two of the lysimeters filled with Volusia silt loam soil are also presented. One of these has been kept bare while the other has been cropped to the rotation already cited. These tanks were filled in 1910 and they have received applications of burnt lime and farm manure. These treatments are summarized in table 1.

Numerous experiments have been conducted in various ways in an attempt to determine the concentration of the soil solution and the extent to which it is affected by growing plants. The literature on this subject has been reviewed rather fully by Stewart (3) who came to the conclusion that the results which have been obtained are contradictory in nature. In analyzing water extracts of thirteen soils of two different types for certain of its constituents through two seasons, Stewart found that during the second season there were notable differences between the concentrations from cropped and uncropped soil, the latter being more concentrated. He also found that there were large differences between the soluble nutrients present in the extracts from uncropped soils.

The writer has found the conclusions drawn by Stewart regarding the greater quantities of nitrates, calcium, potassium and magnesium in the extracts from cropped and uncropped soils, made at various times throughout the year,

to hold for the concentration of soluble material in the percolates from soil tanks.

TABLE 1
Treatment of soil in lysimeters

TANK	SOIL	TREATMENT OF SOIL		
		Fertilizer	Lime	Crop
3	Dunkirk clay loam	Farm manure	None	Rotation
4				Grass
6				None
7	Volusia silt loam	Farm manure	Burnt lime	Rotation
8				Grass
10				None
15	Volusia silt loam	Farm manure	Burnt lime	Rotation
16				None

TABLE 2

Average percolation concentration and loss of soluble material from planted and unplanted lysimeters, filled with Dunkirk clay loam soil, from May 1, 1920 to May 1, 1921

TANK	SOIL TREATMENT	DRAINAGE WATER						SOLIDS REMOVED		TOTAL DRAINAGE	
		May 1-Dec. 1		Dec. 1-Mar. 15		Mar. 15-May 1		Average for two tanks	Per acre		
		Amount	Concen- tration	Amount	Concen- tration	Amount	Concen- tration				
3, 7	Maize	119	358	187	290	69	332	120	660	375	
4, 8	Grass	110	441	163	358	80	372	137	751	353	
6, 10	Bare	378	512	185	406	78	474	305	1,677	641	

TABLE 3

Average percolation, concentration and loss of soluble material from planted and unplanted lysimeters, filled with Dunkirk clay loam soil, from May 1, 1921 to May 1, 1922

TANK	SOIL TREATMENT	DRAINAGE WATER						SOLIDS REMOVED		TOTAL DRAINAGE	
		May 1-Dec. 1		Dec. 1-Feb. 24		Feb. 24-May 1		Average for two tanks	Per acre		
		Amount	Concen- tration	Amount	Concen- tration	Amount	Concen- tration				
3, 7	Oats	96	315	88	256	274	251	122	668	358	
4, 8	Grass	159	389	92	303	296	277	172	944	547	
6, 10	Bare	303	564	115	471	275	581	385	2,120	693	

The concentrations of the drainage water from the lysimeters containing Dunkirk clay loam soil are shown in tables 2, 3 and 4. Each table presents

the results for a single year and for different periods during the year. The periods are quite variable in length since they are dependent on the flow from the planted tanks, which in turn is regulated by climatic conditions and the crop grown. It may be seen at once from the tables that the average concentration of percolates, expressed in parts per million of soluble material, from the bare soils is considerably higher than that from the soils which have been in rotation. The rotation crop for 1920 was maize; for 1921, oats; and for 1922, wheat.

Not only is the concentration of the drainage water from the bare soil greater than that from the planted soil during the growing period of the plant but it continues to be greater year after year for each period shown in the tables. It is interesting to note that the point of lowest concentration for the bare soil percolates each year is greater than the highest concentration for the soil planted to a crop rotation.

TABLE 4

Average percolation, concentration and loss of soluble material from planted and unplanted lysimeters, filled with Dunkirk clay loam soil, from May 1, 1922 to May 1, 1923

TANK	SOIL TREATMENT	DRAINAGE WATER						SOLIDS REMOVED		TOTAL DRAINAGE	
		May 1-Sept. 1		Sept. 1-Mar. 1		Mar. 1-May 1		Average for two tanks	Per acre		
		Amount	Concen- tration	Amount	Concen- tration	Amount	Concen- tration				
3, 7	Wheat	139	244	113	276	249	226	121	667	501	
4, 8	Grass	175	352	119	325	279	234	166	910	673	
6, 10	Bare	336	562	103	481	267	342	330	1,813	706	

After the crop is removed from the planted tanks and with the retarded drainage of the winter months and often its entire absence for several weeks at a time, it would seem that the concentration of the leachings from the cropped soil would be relatively higher as compared with that for the leachings from the bare soil because of the opportunity in point of time for an equilibrium adjustment between the soil material and the soil water. If such an adjustment occurred it most likely would be reflected in the early spring drainage. The absence of such an adjustment is clearly shown by the wide differences in the concentration of the water from the cropped and bare soils for the periods which include the months of March and April. This is in accord with the findings of Hoagland (4) who has presented evidence to oppose the theory that there is an immediate restoration of equilibrium when the soil solution is depleted of its soluble material by the plant or other agency. The data given here would tend to prove that this equilibrium is never reached as long as a crop is allowed to grow on the soil for a portion of each year.

The nitrate nitrogen is always more concentrated in the drainage from the bare soil than in that from the cropped soil. This fact suggests that the greater concentration of total solids in the percolates from the bare soil during the early spring might be attributed to a greater solvent action due to this greater nitrate concentration. However, when the average concentrations of nitrate nitrogen in the leachings from the bare and cropped soils were calculated to calcium nitrate and these values subtracted from the total concentrations of the water for the corresponding soils, the resulting figures, while slightly lower and farther apart than the ones appearing in the tables, showed the percolates to be of the same relative strengths.

Lyon and Bizzell (1) have found that cropping this soil conserved an amount of calcium much greater than the combined conservations of magnesium, sulfur, sodium and potassium. Since phosphates and carbonates are never present in quantities large enough to be of any importance, and since bicarbonates are of about equal strength in the leachings from the cropped and uncropped soils it would seem that most of the nitrate radical would be associated with calcium. In view of these facts the calculation as made above appears justified.

The tables also show that the concentrations of the percolates are more or less independent of the amount of water which passes through the soil. Irrespective of the quantity of drainage from the several tanks, the concentration of that from the bare soil is always highest, that from the soil planted to a crop rotation always lowest, while that from the tanks which are in grass continuously is intermediate. Since the volume of water passing through the tanks is not the determining factor of its concentration it is probable that the soils have reached a stage where a somewhat definite quantity of soluble material is relinquished to the movable water through them and that this quantity is liberated regardless of whether the normal precipitation, which the lysimeters receive, permeates them quickly or slowly.

In most cases the concentration of the percolates are seen to decrease as the seasons progress from the month of May but they regain their former strengths with each succeeding year.

The analyses of the drainage from the Volusia silt loam soil are given in tables 5, 6 and 7. It will not be necessary to point out the facts revealed in these tables beyond the statement that they serve to substantiate the conclusions that have been drawn from the Dunkirk clay loam soil. It may be added, however, that the concentrations of the percolates from the last named soil are higher than those from the Volusia silt loam.

The collective data from the two soils here presented bring out two points rather conclusively: first, that the concentration of the percolates from the lysimeters is not dependent on the quantity of water leaching through the soils; and second, that the different soil treatments result in bringing about a condition within the soils which causes them to liberate their soluble material in a more or less characteristic way.

It is quite possible that the colloidal material in the soil and the water film which is in intimate contact with the soil particles relinquish a rather definite proportional share of their soluble material to that portion of the soil water

TABLE 5

Percolation, concentration and loss of soluble material from planted and unplanted lysimeters, filled with Volusia silt loam soil, from May 1, 1920 to May 1, 1921

TANK	SOIL TREATMENT	DRAINAGE WATER								SOLIDS REMOVED		TOTAL DRAINAGE	
		May 1-Sept. 1		Sept. 1-Dec. 1		Dec. 1-Mar. 15		Mar. 15-May 1		From tank	Per acre		
		Amount	Concen- tration	Amount	Concen- tration	Amount	Concen- tration	Amount	Concen- tration				
15	Maize	158	261	277	243	247	234	127	249	198	1,089	809	
16	Bare	183	482	184	441	181	317	92	322	256	1,408	640	

TABLE 6

Percolation, concentration and loss of soluble material from planted and unplanted lysimeters, filled with Volusia silt loam soil, from May 1, 1921 to May 1, 1922

TANK	SOIL TREATMENT	DRAINAGE WATER								SOLIDS REMOVED		TOTAL DRAINAGE	
		May 1-Oct. 1		Oct. 1-Dec. 1		Dec. 1-Feb. 24		Feb. 24-May 1		From tank	Per acre		
		Amount	Concen- tration	Amount	Concen- tration	Amount	Concen- tration	Amount	Concen- tration				
15	Oats	130	254	331	240	273	212	448	205	262	1,442	1,182	
16	Bare	205	390	295	420	299	250	441	279	404	2,223	1,240	

TABLE 7

Percolation, concentration and loss of soluble material from planted and unplanted lysimeters filled with Volusia silt loam soil, from May 1, 1922 to May 1, 1923

TANK	SOIL TREATMENT	DRAINAGE WATER								SOLIDS REMOVED		TOTAL DRAINAGE	
		May 1 Sept. 1		Sept. 1 Mar. 1		Mar. 1-May 1		From tank	Per acre				
		Amount	Concen- tration	Amount	Concen- tration	Amount	Concen- tration		gm.	lbs.			
15	Wheat	458	248	431	242	345	182	281	1,545	1,234			
16	Bare	564	376	358	282	285	225	377	2,074	2,074		1,207	

which is free to move. This assumption would help to explain why the concentration of the soil solution, as measured by Bouyoucos and McCool (5) and others, differs from that ordinarily found in soil extracts and in the drainage water from lysimeters.

REFERENCES

- (1) LYON, T. LYTTLETON, AND BIZZELL, JAMES A. 1918 Lysimeter experiments. Records for tanks 1 to 12 during the years 1910 to 1914 inclusive. Cornell Univ. Agr. Exp. Sta. Mem. 12.
- (2) LYON, T. LYTTLETON, AND BIZZELL, JAMES A. 1921 Lysimeter experiments II. Records for tanks 13 to 16 during the years 1913 to 1917 inclusive. Cornell Univ. Agr. Exp. Sta. Mem. 41.
- (3) STEWART, GUY R. 1918 Effect of season and crop growth in modifying the soil extract. *In* Jour. Agr. Res., v. 12, p. 311-368.
- (4) HOAGLAND, D. R. 1918 The freezing-point method as an index of variations in the soil solution due to season and crop growth. *In* Jour. Agr. Res., v. 12, p. 369-395.
- (5) BOYOUCOS, G. J., AND MCCOOL, M. M. 1915 The freezing point method as a new means of measuring the concentration of the soil solution directly in the soil. Mich. Agr. Exp. Sta. Tech. Bul. 24.

STUDIES ON VIRGIN AND DEPLETED SOILS¹

C. E. MILLAR^{2,3}

Wisconsin Agricultural Experiment Station

Received for publication September 22, 1923

The actual changes in several important respects which a soil undergoes in passing from a virgin to a depleted condition have not been investigated to any great extent.

It is quite generally conceded that the supply of available plant food elements as well as the content of organic matter is materially decreased as a soil becomes "worn out." A number of cases have also been reported in which the total amounts of phosphorus and calcium have been reduced.

So far as the writer is aware, however, little information is at hand regarding the relative rate of change in the concentration of the soil solution of depleted and virgin soils when they are maintained at a given moisture content and temperature for various periods. The composition of solutions so obtained is unknown as well as the relative ability of virgin and badly run down soils to repeatedly give up solutes when the material in solution is removed by washing. The rôle of organic matter in maintaining the concentration of the soil solution is also uninvestigated. It is the purpose of this paper to throw some light on these questions and to set forth any relationships found to exist between the amounts of various plant food elements going into solution from a number of soils upon standing different lengths of time at different moisture contents, and the increase in plant growth resulting from addition of these elements.

REVIEW OF LITERATURE

McCool and Millar (3) determined the rate of formation of soluble material in several virgin and the corresponding depleted soils by means of the freezing point method. In general the concentration of the soil solution of the virgin soils was much greater than that of the cropped soils after a ten-day period at 25°C. At the expiration of thirty days, however, the difference had largely disappeared. A decrease in moisture content and a lower temperature also tended to decrease the difference in rate of solubility.

¹ Abstract of a thesis submitted at the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy. Published with the permission of the Director of the Wisconsin Agricultural Experiment Station.

² The writer desires to express his appreciation to Prof. E. Truog for many helpful suggestions and criticisms.

³ Associate Professor of Soils, Michigan Agricultural College.

Millar (5) reported a correlation between the difference in rate of solution of several depleted and virgin soils and the observed differences in productiveness. The samples were washed on ordinary filters to remove the major portion of the soluble salts before placing in the constant temperature chamber. This procedure reduced the tendency, previously reported, for the concentrations of the solutions to decrease as the period of contact was prolonged.

Shedd (8) found the total phosphorus and that soluble in 0.2 N HNO₃ to be greater in seventeen virgin soils than in the corresponding cropped samples.

As the result of a careful study of the phosphorus content of nine soils which had been under cultivation for 40-60 years and of corresponding virgin soils Whitson and Stoddart (12) report large losses as the result of cropping with the exception of one case. Other soils which had received large amounts of manure during cultivation of 30-62 years showed large increases in phosphorus content in a number of cases, but more than half of these contained more phosphorus in the virgin than in the cropped and manured samples.

Shedd (9) divided the soils of Kentucky into areas on a geological basis and determined the total calcium and that soluble in 0.2 N HNO₃ and in carbonated water in samples of cropped and virgin soils from each area. In the large majority of cases each method showed more calcium in the virgin than in the cropped soils.

Swanson and Miller (10) report the analyses of samples from long cropped areas and areas in native bluestem hay or buffalo grass pasture from several types of Kansas soils. In only two cases, however, were the cropped and virgin samples taken from areas in close proximity. The data for the two comparable soils show a decided loss in sulfur, nitrogen and carbon as a result of cropping. One shows a gain in phosphorus, one a loss of potassium and both a gain in calcium. An average of the data for all the soils shows a marked decrease in sulfur, nitrogen and carbon content and an increase in potassium and very little change in phosphorus and calcium. As a whole the results are rather unusual.

COLLECTION OF SAMPLES

The samples in general represent the surface stratum 6 to 7 inches in depth. In some cases the sampling extended to the depth of the darker colored surface soil which in some virgin timbered soils was less than 6 inches while in some sandy cultivated soils it was more.

Two samples were taken from every soil. One from a field which had been under cultivation for a considerable period of years and had decreased more or less in productivity. The other was taken from a piece of woodland or from an old line fence row which was only a short distance from the site of the first sample. The first sample is designated as cropped or depleted while the latter is referred to as the virgin or uncropped soil. Thus the two samples represent the same soil type, the only difference between them being the changes resulting from the growth and partial removal of common farm crops, in one case, and from the growth without removal of more or less virgin vegetation in the other.

The samples were taken to the laboratory, air-dried and passed through a 2 mm. screen to remove pebbles and the coarser organic material. They were then stored in suitable containers until utilized in the laboratory experiments.

The soils studied were collected from six counties in Michigan and include eleven silt loams, seventeen sandy loams, five loams, thirteen loamy sands, and two clay loams. They represent the predominating soil types in the counties sampled.

RATE OF SOLUTION OF VIRGIN AND CROPPED SOILS

The first part of the work was devoted to the study of the rate of increase in concentration of the soil solution when the samples were washed practically free of soluble salts and then maintained at a uniform temperature with a water content slightly above saturation.

TABLE 1

Rate of solution of virgin and cropped soils expressed as freezing point depressions

SOIL NUMBER	CONDITION	DAYS MAINTAINED AT 25°C.							
		0	1	2	6	10	20	40	60
<i>Silt loams</i>									
1	Cropped	°C.	°C.	°C.	°C.	°C.	°C.	°C.	°C.
	Virgin	0.001 0.004	0.001 0.004	0.009 0.010	0.011 0.020	0.012 0.040	0.013 0.043	0.026 0.074	0.033 0.081
2	Cropped	0.000	0.009	0.010	0.013	0.026	0.029	0.038	0.017
	Virgin	0.000	0.009	0.013	0.024	0.052	0.064	0.059	0.045
6	Cropped	0.000	0.003	0.004	0.009	0.007	0.020	0.032	0.022
	Virgin	0.000	0.009	0.013	0.020	0.042	0.053	0.060	0.041
7	Cropped	0.000	0.005	0.005	0.010	0.010	0.020	0.043	0.023
	Virgin	0.000	0.009	0.013	0.020	0.042	0.053	0.060	0.041
<i>Sandy loams</i>									
14	Cropped	0.000	0.001	0.003	0.012	0.028	0.025	0.009	0.009
	Virgin	0.000	0.002	0.008	0.015	0.029	0.024	0.013	0.015
15	Cropped	0.000	0.001	0.003	0.006	0.012	0.020	0.010	0.012
	Virgin	0.000	0.001	0.021	0.034	0.045	0.049	0.021	0.025
16	Cropped	0.000	0.002	0.001	0.008	0.010	0.006	0.012	0.013
	Virgin	0.001	0.001	0.009	0.021	0.039	0.045	0.056	0.041
18	Cropped	0.000	0.003	0.011	0.011	0.007	0.051	0.071	0.057
	Virgin	0.000	0.006	0.013	0.025	0.030	0.079	0.070	0.052
21	Cropped	0.000	0.001	0.006	0.013	0.025	0.041	0.066	0.036
	Virgin	0.000	0.007	0.012	0.022	0.030	0.050	0.077	0.078
<i>Loamy sands</i>									
28	Cropped	0.000	0.001	0.002	0.003	0.015	0.015	0.010	0.007
	Virgin	0.000	0.008	0.003	0.023	0.030	0.033	0.026	0.027
30	Cropped	0.000	0.001	0.002	0.002	0.004	0.009	0.016	0.009
	Virgin	0.000	0.009	0.018	0.029	0.039	0.049	0.054	0.044
31	Cropped	0.000	0.001	0.001	0.001	0.002	0.001	0.006	0.001
	Virgin	0.000	0.011	0.019	0.035	0.043	0.063	0.067	0.054
33	Cropped	0.000	0.001	0.001	0.001	0.002	0.002	0.002	0.002
	Virgin	0.001	0.002	0.003	0.010	0.011	0.013	0.023	0.012

TABLE 1—Continued

SOIL NUMBER	CONDITION	DAYS MAINTAINED AT 25°C.							
		0	1	2	6	10	20	40	60
<i>Loams</i>									
41	Cropped	0.000	0.002	0.008	0.014	0.020	0.029	0.035	0.037
	Virgin	0.000	0.002	0.011	0.020	0.027	0.028	0.030	0.033
42	Cropped	0.000	0.007	0.010	0.018	0.020	0.030	0.035	0.020
	Virgin	0.000	0.011	0.019	0.033	0.046	0.055	0.068	0.059
43	Cropped	0.000	0.001	0.001	0.004	0.011	0.012	0.027	0.030
	Virgin	0.000	0.012	0.015	0.030	0.040	0.060	0.059	0.041

It was decided to use the freezing point method of Bouyoucos and McCool (2) since this permitted rapid determination of the concentration of the soil solution directly in the soil without necessitating discarding the sample.

The procedure was as follows:

About 60 gm. of the air dry sample was placed in an ordinary filter and washed with distilled water until practically free of soluble material as indicated by the freezing point method. After draining for an hour or so the soil was removed and thoroughly mixed by stirring in a tumbler. Samples were placed in freezing point tubes which were then stoppered and placed in a constant temperature chamber at 25°C. This procedure left the samples with a moisture content such that after settling, a column of water from an eighth to a quarter of an inch deep appeared above the soil. This condition was considered much more comparable for the different soil classes than the method of adding a given volume of water to a definite weight of soil.

The tubes were taken from the chamber every week or ten days during the period of the experiment, the stoppers removed and the contents thoroughly stirred to allow the escape of any gases which might have formed.

Freezing point determinations were made immediately after the samples were washed and placed in the tubes and at frequent intervals thereafter. The freezing point depressions for representative samples are presented in table 1.

The data show that the virgin soils possess the power of giving up soluble material at a greater rate than the corresponding cropped soils. The divergence between the cropped and virgin samples in this respect is quite variable as would be expected since the degree of depletion in the different soils is quite different.

In most cases the greatest concentration obtained was considerably higher in the case of the virgin than of the cropped samples.

The tendency exhibited principally by the heavier soils to reach a maximum concentration of solution after 20–40 days and then decrease is undoubtedly due in part at least to the action of anaerobic organisms. It also seems highly probable that as hydrolysis and solution proceeded, changes may have occurred which resulted in precipitation of some of the dissolved salts. The possibility of adsorption should also be considered.

SOLUBILITY OF SUBSOILS FROM CROPPED AND VIRGIN AREAS

The finding of such a decrease in rate of solubility of surface soils as a result of continuous cropping at once suggests the question as to what effect depletion has on the solubility of the lower stratum or subsoil. To gain some information on this point a few subsoils were washed free of soluble salts, placed in freezing point tubes and maintained at 25°C. as outlined above. The freezing point depressions found at different times during the period of the experiment are shown in table 2.

It is surprising to note that these data show no appreciable difference in the rate of solubility of the subsoils from the depleted and virgin soils. In fact the solubility of all the samples is very slight. This agrees with the results of McCool and Millar (4) who determined the rate of solubility of subsoils collected from regions of great diversity of climatic conditions and found with few exceptions, a very low rate of solution.

TABLE 2

Rate of solution of virgin and cropped subsoils expressed as freezing point depressions

SOIL CLASS	CONDITION	DAYS MAINTAINED AT 25°C.					
		0 °C.	1 °C.	5 °C.	20 °C.	40 °C.	60 °C.
Very fine sandy loam	Cropped	0.000	0.001	0.002	0.002	0.002	0.000
	Virgin	0.000	0.002	0.003	0.002	0.002	0.000
Sandy loam	Cropped	0.000	0.000	0.004	0.006	0.009	0.006
	Virgin	0.000	0.003	0.008	0.012	0.010	0.007
Silt loam	Cropped	0.000	0.001	0.003	0.001	0.002	0.000
	Virgin	0.000	0.004	0.006	0.002	0.003	0.004
Silt loam	Cropped	0.000	0.000	0.004	0.007	0.006	0.007
	Virgin	0.000	0.000	0.013	0.020	0.021	0.018

RELATIVE ABILITY OF CROPPED AND VIRGIN SOILS TO RENEW THE CONCENTRATION OF THE SOLUTION AFTER REMOVAL OF SOLUBLE SALTS BY WASHING

Bouyoucos (1) found that soils maintained at 53°C. had a more rapid rate of solubility than at room temperature. A preliminary experiment by the writer showed that soils washed free of soluble salts and then maintained at 50°C. with a moisture content slightly above saturation develop a rather high concentration of solution after forty hours. The virgin samples also showed a greater concentration than the corresponding cropped soils. It was deemed proper, therefore, to use this temperature and period of contact in the present experiment.

The soils were washed free of soluble salts on filters as previously described, then thoroughly mixed and quite large samples placed in freezing tubes. The tubes were stoppered and placed in the oven at 50°C. for forty hours, after which the freezing point depressions were determined and the soil again washed free of salts on small porcelain filters. The samples were made up to the proper moisture content and again placed in the oven for forty hours. This procedure was repeated several times. The data are presented in table 4.

TABLE 4

Relative ability of cropped and virgin soils to give up soluble material after successive washings to remove soluble salts shown by freezing point depressions

SOIL	CONDITION	FIRST PERIOD	SECOND PERIOD	THIRD PERIOD	FOURTH PERIOD	FIFTH PERIOD
Fine sandy loam	Cropped	0.011	0.008	0.010	0.008	0.007
	Virgin	0.032	0.016	0.020	0.016	0.027
Silt loam	Cropped	0.011	0.002	0.008	0.004	0.007
	Virgin	0.028	0.019	0.025	0.020	0.017
Sandy loam	Cropped	0.025	0.013	0.013	0.013	
	Virgin	0.030	0.014	0.021	0.025	
Loamy sand	Cropped	0.019	0.001	0.004	0.002	0.001
	Virgin	0.044	0.021	0.022	0.018	0.020
Sandy loam	Cropped	0.014	0.003	0.002	0.003	0.005
	Virgin	0.027	0.011	0.011	0.008	0.013
Silt loam	Cropped	0.025	0.008	0.008	0.006	0.013
	Virgin	0.038	0.018	0.016	0.014	0.018
Loamy sand	Cropped	0.007	0.001	0.000	0.001	0.002
	Virgin	0.030	0.013	0.012	0.010	0.015

The results show that after the material going into solution during the first period is removed the depleted soils show only a feeble power to give up salts. It is interesting to note, however, that the concentration produced at each successive incubation is practically the same. This is in accord with the general observation that a soil will decline to a certain state of depletion and then continue to produce about the same yield from year to year. The productivity may, therefore, be taken as a measure of the rate of weathering of the less readily attacked minerals or the rate at which they give up soluble salts.

The virgin samples also show a decreased ability to give up soluble salts after the removal of the material liberated during the first period of incubation. Like the depleted sample the solutions also attain approximately the

same concentration at each succeeding incubation. The striking fact is that the concentration reached each time is much higher than is that of the corresponding depleted sample. This fact would lead one to predict the difference in productivity which exists.

EFFECT OF REMOVAL OF ORGANIC MATTER BY OXIDATION WITH HYDROGEN PEROXIDE ON SOLUBILITY OF CROPPED AND VIRGIN SOILS

Peterson (7) found that oxidation of the organic matter of surface soils with hydrogen peroxide resulted in an increased amount of phosphorus, iron, and aluminum soluble in 0.2 *N* HNO₃ but not of calcium or manganese. Treatment of subsoils showed no increase in the solubility of phosphorus. His conclusion was that phosphorus, iron, and aluminum are held in organic complexes and that the mineral particles of the soil are not affected by the oxidation process. It was decided, therefore, to determine the effect of removal of the organic matter by this method on the rate of solubility in water of the soils under consideration.

The procedure followed was to place 60 gm. of soil in an Erlenmeyer flask and add sufficient 3 per cent chemically pure peroxide to cover the soil. The contents of the flasks were thoroughly agitated every few hours and when the action had ceased enough 30 per cent peroxide was added to restore the liquid to approximately 3 per cent strength. When no further reaction was visible at room temperature the flasks were placed in a water bath at 30°C. and the above procedure repeated until practically all the organic matter was destroyed. The soils were now washed on filters with distilled water to free them of soluble materials after which they were thoroughly mixed and samples placed in freezing point tubes. These samples were maintained at 30°C. and freezing point determinations made after periods of 3, 7, 21 and 35 days. As controls, samples of the soils were given the same treatment as just outlined excepting that the peroxide was omitted. The data are found in table 5.

These results are very significant. In no case does the soil from which the organic matter has been removed show a lower rate of solubility than the corresponding untreated sample. On the other hand three of the soils show a distinctly higher rate of solubility and others a tendency for greater solubility when the organic matter is removed. This would seem to indicate that the organic matter, in place of being either the source of soluble material or the liberating agent, in reality retards the liberation of soluble salts. This seems plausible since the so-called humus is known to form a coating around the mineral particles and this may act as a protecting agent. In fact microscopical examination of some of the soils before and after treatment with peroxide showed the mineral particles to be much lighter colored in the treated samples. It must be recognized, however, that the soluble salts given up before removal of the organic matter may come largely from the organic material while after the removal of the organic coating fresh surfaces of the

mineral particles are exposed which have an even greater rate of solution. This is comparable to the finding of a decreased lime requirement of soils as the result of grinding.

The difference in rate of solubility between the cropped and virgin samples from which the organic matter had been removed was generally greater after the removal of the organic matter than before. This is very interesting inasmuch as it discredits the view occasionally expressed that soil depletion consists primarily in the loss of the major portion of the organic matter.

TABLE 5

Effect of removal of organic matter by H_2O_2 on the rate of solution of cropped and virgin soils shown by freezing point depressions

SOILS	CONDITION	DAYS MAINTAINED AT 30°C.									
		0		3		7		21		35	
		Normal	Treated	Normal	Treated	Normal	Treated	Normal	Treated	Normal	Treated
Sandy loam	Cropped	0.000	0.000	0.000	0.005	0.004	0.017	0.005	0.035	0.014	0.034
	Virgin	0.000	0.008	0.005	0.006	0.007	0.023	0.030	0.031	0.029	0.031
Silt loam	Cropped	0.000	0.000	0.018	0.017	0.022	0.028	0.044	0.044	0.043	0.041
	Virgin	0.002	0.000	0.020	0.018	0.026	0.057	0.049	0.075	0.038	0.070
Fine sandy loam	Cropped	0.003	0.010	0.018	0.020	0.019	0.018	0.034	0.038	0.037	0.042
	Virgin	0.005	0.000	0.018	0.024	0.022	0.061	0.046	0.056	0.040	0.050
Loamy sand	Cropped	0.000	0.000	0.000	0.009	0.003	0.009	0.017	0.019	0.018	0.019
	Virgin	0.000	0.003	0.010	0.018	0.012	0.019	0.024	0.025	0.025	0.030

COMPOSITION OF MATERIAL GOING INTO SOLUTION FROM CROPPED AND VIRGIN SOILS

The next point of interest is to determine the differences in chemical composition of the soluble material going into solution from cropped and virgin soils.

The procedure followed was to place 2000 gm. of air dry soil in an aspirator bottle and stopper with a one-hole rubber stopper over which a small pad of glass wool was placed as a filter. The bottle was then inverted and water added through the tubulation and allowed to percolate through the soil until most of the soluble salts were removed. The hole in the rubber stopper was then closed and enough water added to slightly more than cover the soil. After standing at room temperature for three weeks the plug was removed from the stopper and the solution allowed to drain out. The soil was then washed by adding successive portions of distilled water and allowing it to percolate through. Solution and washings were thoroughly mixed

and aliquots used for analysis. The results in terms of parts per million of air dry soil appear in table 6.

These data bring out some interesting points. With one exception the depleted soils show a decidedly higher content of soluble sulfates. This is doubtless the result of the application of farmyard manure at various times during the period of cultivation. It would indicate that on these soils at least sulfur has not as yet become a limiting element in plant growth.

The results for chlorine are somewhat more variable as four of the soils show larger quantities in the virgin samples, two in the cropped samples

TABLE 6

Material going into solution from cropped and virgin soils upon standing 21 days at room temperature with high water content

SOIL	CONDITION	Ca(HCO ₃) ₂	Cl	Fe ₂ O ₃ + Al ₂ O ₃	Ca	Mg	SO ₄	P
Sandy loam	Cropped	109.35	12.59	2.95	6.75	2.21	13.66	1.08
	Virgin	341.70	18.89	8.02	17.75	6.75	5.03	0.80
Very fine sandy loam	Cropped	396.39	37.79	2.95	26.35	6.84	11.08	0.77
	Virgin	410.05	31.49	6.33	22.75	7.14	0.47	0.74
Silt loam	Cropped	177.65	6.30	18.14	11.00	3.23	12.67	0.71
	Virgin	628.75	6.30	30.80	43.00	7.30	6.08	0.74
Silt loam	Cropped	82.00	6.30	1.69	5.25	2.43	10.92	2.48
	Virgin	369.05	9.44	16.45	21.25	8.97	1.39	0.80
Loamy sand	Cropped	4.35	7.20	2.70	29.25	7.51	10.48	0.30
	Virgin	16.40	12.22	7.50	89.72	19.91	7.02	0.42
Sandy loam	Cropped	5.19	24.49	3.60	34.45	9.54	6.72	0.35
	Virgin	9.11	9.79	33.30	67.29	12.53	7.38	0.56
Loamy sand	Cropped	2.23	9.79	2.40	14.10	5.38	12.27	0.35
	Virgin	8.91	26.95	4.55	48.72	14.39	9.48	0.69

* Parts per million based on air dry soil.

and no difference in the other case. The amount of soluble phosphorus is also so variable that it cannot be stated that a decrease in amount of water soluble phosphorus results from many years of cropping.

Of the remaining determinations including alkalinity, iron and aluminum, calcium and magnesium the results without exception show larger quantities going into solution from the virgin soils. The decrease in soluble alkaline earths might be predicted as a result of increased leaching due to cultivation. The decrease in soluble iron and aluminum, however, was scarcely to be expected inasmuch as it has been shown that an increase in soil acidity is often accompanied by an increase in solubility of these elements.

RELATION OF THE RESPONSE OF SOILS TO FERTILIZER TREATMENT WITH
THE AMOUNTS OF NUTRIENTS IN THE SOIL SOLUTION

Inasmuch as the variations in the composition of the solutions from depleted and virgin soils were not as great as might be expected it was decided to determine if any relation exists between the response to an application of any element or combination of elements and the amounts of such constituents in the soil solution.

Two methods of obtaining the soil solution were employed. The first was by displacement with alcohol as described by Parker (6). The second procedure consisted in allowing the soils to stand eighteen days at room temperature with water in the ratio of one part of air dry soil to three parts of water. The containers were thoroughly shaken every day. The clear solution was obtained by filtering with a Buchner funnel.

The filtrates were analyzed for phosphorus, potassium, calcium, and magnesium and the results calculated to parts per million of air dry soil. The data appear in table 10 together with the greenhouse results.

In the case of the mineral soils it is seen that the soils which yielded the most calcium and magnesium by either method of extraction gave negative or very small returns as the result of treatment with calcium carbonate.

The amounts of phosphorus in the soil solution obtained by both methods were quite small but show some correlation with the increase of plant growth due to addition of this element. The correlations are better when the results from the dilution method are considered.

The data for potash show little correlation when the results from the displacement method are considered. When the dilution method was used, however, the amounts of the element extracted correlate rather closely with the response of alfalfa to addition of potassium. Soil 127 is something of an exception to this but it should be noted that this soil was productive without fertilizer treatment. The decreased growth resulting from additions of potassium alone in the case of two of the sands is doubtless due to an increase of active acidity as a result of the addition of the potassium salt.

In the case of the peat soils the results from neither method of extraction correlate well with the response in plant growth due to addition of the plant food elements.

Inasmuch as the data just presented show that the dilution method indicates the need of the soil for plant food elements much better than the displacement method it was considered probable that a method involving a larger proportion of water to soil and a shorter period of contact would be still more satisfactory. Accordingly samples were prepared using five parts of water to one of soil in the case of mineral soils, and seven and one-half of water to one of soil for the peats. The samples were allowed to stand twenty hours at room temperature and then filtered. The results of the determinations on the filtrate are found in table 11.

TABLE 19
Relation of mineral elements in the soil solution to response of soils to fertilizer treatments

SOIL CLASS	Displacement method						Elution method						Total weight of check gm.	Increase due to addition of WEIGHT OF DRY ALFALFA (3 CROPS)					
	Ca	Mg	P	K	Ca	Mg	P	K	Ca	Mg	P	K		CaCO ₃	$\Sigma + P$ (CaCO ₃)	gm.	gm.		
Silt loams.....	253	112.0	48.4	5.6	150.0	89.0	5.0	3.4	36.00	11.95	-6.25	21.98	36.00	-4.52	24.03	gm.	gm.		
	127	31.3	8.5	5.0	6.2	129.0	40.3	6.6	10.9	57.72	5.43	2.73	9.78						
	141	43.9	10.5	4.7	5.4	97.0	20.1	4.1	8.0	20.80	2.20	12.15	18.53						
	225	65.1	33.2	6.1	3.2	172.0	84.3	4.5	7.7	46.73	3.77	2.77	24.79						
Fine sandy loam.....	239	29.3	11.2	4.3	2.9	41.5	17.7	2.7	2.5	19.93	10.47	10.92	25.72	4.20	25.80	gm.	gm.		
	71	39.4	10.4	7.3	19.5	67.0	26.4	19.6	8.9	51.15	3.25	5.35	0.07						
Sands.....	85	29.3	3.4	2.1	2.6	50.0	17.4	14.7	6.6	60.77	1.68	0.68	1.10	-0.72	0.90	17.65	gm.	gm.	
	296	10.0	3.9	3.0	1.4	15.0	12.1	2.9	6.4	30.05	-1.50	7.35	10.17						
	281	7.0	2.6	1.2	2.3	29.0	2.9	6.8	4.2	22.75	-4.40	7.05	15.35						
Peats.....	337	42.7	238.4	26.7	41.0	1056.0	471.9	50.0	61.5	52.49	2.06	11.51	35.31	-5.59	32.31	31.17	gm.	gm.	
	309	82.3	54.9	20.8	15.3	66.0	56.6	30.0	17.3	38.12	1.68	3.58	17.60						
	267	76.8	27.3	18.8	35.3	102.0	48.3	35.7	52.8	28.48	5.32	14.57	16.82						

TABLE 11
Relation of mineral elements extracted from soils by water to response to fertiliser treatments

SOIL CLASS	NUMBER	SOIL SOLUTION			ACIDITY OF SOIL	TOTAL P CONTENT per cent	WEIGHT OF 3 CROPS OF ALFALFA kg.	HISTORY OF SOILS	
		Ca ppm.	P ppm.	K ppm.				CROPPED 1 year. Crops poor Virgin soil. Good volunteer clover Cropped 20 years—has received considerable manure— yields decreasing	CROPPED 1 year. Crops poor Virgin soil. Good volunteer clover Cropped 20 years—has received little manure— legumes fail No history available
Silt loam.....	253	180.0	14.2	11.6	Not acid	0.10	36.00	CROPPED 1 year. Crops poor Virgin soil. Good volunteer clover Cropped 20 years—has received considerable manure— yields decreasing	CROPPED 1 year. Crops poor Virgin soil. Good volunteer clover Cropped 20 years—has received little manure— legumes fail No history available
	127	72.5	24.3	26.6	Medium	0.034	57.72		
	141	55.0	15.3	10.1	Strong	0.047	20.80		
Silt loam.....	225	112.5	16.0	6.4	Very slight	0.090	46.73	CROPPED 1 year. Crops good on this part of field Same field as 225—crops do poorly on this part of field and legumes fail	CROPPED 1 year. Crops good on this part of field Same field as 225—crops do poorly on this part of field and legumes fail
	239	42.5	5.3	9.8	Strong	0.066	19.93		
Fine sandy loam.....	71	45.0	21.4	25.6	Medium		51.15	CROPPED 1 year. Good volunteer clover Virgin. Good growth of clover Cropped 20 years—has received little manure— legumes fail No history available	CROPPED 1 year. Good volunteer clover Virgin. Good growth of clover Cropped 20 years—has received little manure— legumes fail No history available
	85	85.0	16.0	18.3	Slight	0.042	60.77		
	296	27.5	5.1	8.7	Medium	0.023	30.05		
Sands.....	281	30.0	5.8	9.8	Medium	0.023	22.75	CROPPED 1 year. Grew 100 bushels of corn after being manured and fertilized—cropped 1 year Cropped 3 years—had 1 ton of lime and some ferti- lizer—crops fair In blue joint grass 30 years	CROPPED 1 year. Grew 100 bushels of corn after being manured and fertilized—cropped 1 year Cropped 3 years—had 1 ton of lime and some ferti- lizer—crops fair In blue joint grass 30 years
	337	145.3*	13.4	16.8	Not acid	0.085	52.49		
	309	31.9	2.8	8.7	Strong	0.11	38.12		
Peats.....	267	16.8	6.0	15.2	Very strong	0.141	28.48	CROPPED 1 year. In blue joint grass 30 years	CROPPED 1 year. In blue joint grass 30 years

* Data for peats have been divided by four to correct for difference in volume weight between peats and mineral soils.

These results show some rather remarkable correlations. Considering first the silt loams it is seen that whenever a large amount of calcium is extracted the yields of alfalfa are large even though the amounts of phosphorus and potassium in the soil solution are small. On the other hand when the amount of calcium going into solution is not unusually large but the concentrations of phosphorus and potassium are high the yield is also quite large. This is exemplified by soil 127.

It is also of interest to note that the amounts of calcium dissolved by this method correlate more closely with the acidity as determined by the Truog method than do the amounts of calcium found in the soil solution by the displacement method. It is noteworthy that the amounts of phosphorus extracted by this method do not correlate with the total phosphorus present.

The sandy soils exhibit the same characteristics noted above. Number 85 showed a high solubility of calcium, phosphorus and potassium and produced a large yield of alfalfa while the other two sands showed a mediocre solubility of these elements and also indifferent growth of alfalfa.

In the case of the peat soils number 337 is outstanding in the amount of the three plant food elements going into solution and also in the yield of alfalfa. Soil 309 has a low solubility of phosphorus and potassium but a comparatively high solubility of calcium and shows a medium growth of crop. Soil 267 shows a considerably higher solubility of phosphorus and potassium than soil 309 but a much lower solubility of calcium and also a somewhat less growth of alfalfa.

The results for the soils as a whole are extremely interesting. In several instances they lend support to the explanation of the difference in feeding power of plants given by Truog (11) to the effect that alfalfa may feed readily on a low concentration of phosphorus and potassium if sufficient lime is present. In cases where the amount of lime is limited a higher concentration of the other elements is necessary for satisfactory growth.

A point strongly emphasized by the greenhouse tests is that in interpreting the results of greenhouse or plat tests the data from all the treatments must be considered in order to determine whether or not a soil is in need of any particular element or treatment. This is well illustrated by soil number 253. When phosphorus alone was applied to this soil the yield was decreased but when phosphorus and potassium were both used the increase was almost double that obtained when potassium was applied alone. Calcium carbonate also decreased the yield when used alone but in conjunction with phosphorus and potassium the growth of alfalfa was greater than on the pot receiving a combination of phosphorus and potassium without lime.

Soil 309 lends support to the points brought out above. The increased yield from an application of both phosphorus and potassium is much greater than one would be led to expect from the increase noted when these elements were applied singly. The increased growth of alfalfa on the pot receiving phosphorus, potassium and lime was also somewhat greater than might be

anticipated from the meager increase due to lime alone and the combined effects of phosphorus and potassium.

More exact conclusions regarding the needs of these soils could have been drawn had the treatment included combinations of phosphorus and lime and potassium and lime. Under those conditions the need or response to phosphorus could be determined by comparing the results from the potassium lime treatment with the phosphorus, potassium lime treatment. Similarly the effects of potassium could be determined by comparison of results from the phosphorus lime treatment with those from the potassium phosphorus lime treatment.

The interpretation of the results of the tests is somewhat complicated by the fact that disodium phosphate was used as a source of phosphorus. Inasmuch as this salt may decrease acidity somewhat the results from its application may be due in part to this factor as well as to the addition of phosphorus.

Considering all the data from the various methods of extraction employed and the solubility measurements made by the freezing point method, it appears that the rate of solution of calcium and other plant food elements is in reality the important factor rather than the total amounts in the soil solution at any given time.

SUMMARY

A study of forty-eight depleted and the corresponding virgin soils showed the latter to have a greater rate of solubility, as measured by the freezing point method, when maintained at 25°C. with a moisture content somewhat above saturation. The fact that a considerable number of soils were studied and rather uniform results were secured would seem to warrant a rather general conclusion that a decrease in rate of solubility is one of the important changes a soil undergoes in passing from a virgin to a more or less depleted condition.

An equal or greater rate of solution was observed in several soils after removal of the organic matter by treatment with hydrogen peroxide than in the untreated samples. The difference in rate of solubility between cropped and virgin soils from which the organic matter had been removed by means of hydrogen peroxide was generally greater than in the untreated samples. These results lead to the conclusion that the larger supply of organic matter generally present in virgin soils may not necessarily be the cause of their greater rate of solubility.

The solubility of a number of subsoils was found to be very low compared to the surface soils. It was also found that subsoils from depleted areas had as great a solubility as subsoils from the corresponding virgin soils. This leads to the conclusion that most crop plants feed primarily in the surface or plowed stratum of the soil.

The amounts of various materials going into solution from depleted and virgin soils maintained for three weeks at room temperature with a moisture

content somewhat above saturation were determined. With one exception, the cropped soils yielded more sulfates while the virgin soils gave the larger amounts of iron, aluminum, calcium, and magnesium. Phosphates and chlorides were given up in larger quantities by the virgin soils in some cases and by the cropped soils in other cases.

Comparisons were made of the yields of alfalfa on untreated soils and soils receiving applications of calcium carbonate and various plant food elements alone and in combination with the amounts of various nutrients in the soil solution obtained by three different methods.

When the displacement method was used a fair correlation was noted between the amounts of calcium and phosphorus in the soil solution from several silt loams and the response of plant growth to addition of these elements. The data for the sandy soils used do not show such a good correlation and little or no correlation was found in the case of several peat soils. The amounts of potassium in the solutions showed little relation to the response of plant growth to addition of potassium in any of the soil classes.

When the soils were extracted with three parts of water to one of soil by weight with a period of contact of eighteen days fair correlations were observed in so far as phosphorus and calcium are concerned in both the silt loam and sandy classes. Also more consistent relations with respect to potassium were found than when the displacement method was used. The results for the peat soils showed practically no correlation.

The total amounts of material found in the extracts agree quite well with the growth of alfalfa produced on the check pots.

When the soils remained in contact with larger proportions of water (one to five for the mineral soils and one to seven and one-half for the peats) for twenty hours, the total amounts of material extracted show a very remarkable correlation with the yields of alfalfa produced on the untreated soil.

In cases where comparatively large amounts of calcium went into solution but only small quantities of phosphorus and potassium the growth of alfalfa was quite satisfactory, thus indicating that a highly available lime supply may render adequate small amounts of these elements.

The data as a whole indicate that the rate at which various materials are given up by soils is a very important factor in determining their crop producing capacity. Studies along this line are being extended.

REFERENCES

- (1) Bouyoucos, G. J. 1919 Rate and extent of solubility of soils under different treatments and conditions. Mich. Agr. Col. Exp. Sta. Tech. Bul. 41.
- (2) Bouyoucos, G. J., AND McCool, M. M. 1915 The freezing point method as a new means of measuring the concentration of the soil solution directly in the soil. Mich. Agr. Col. Tech. Bul. 24.
- (3) McCool, M. M., AND MILLAR, C. E. 1918 Soluble salt content of soils and some factors affecting it. Mich. Agr. Col. Exp. Sta. Tech. Bul. 43.

- (4) McCOOL, M. M., AND MILLAR, C. E. 1920 The formation of soluble substances in soils taken from widely separated regions. In *Soil Sci.*, v. 10, p. 219-235.
- (5) MILLAR, C. E. 1919 The comparative rate of formation of soluble material in cropped and virgin soils as measured by the freezing point method. In *Soil Sci.*, v 7, p. 253-257.
- (6) PARKER, F. W. 1921 Methods of studying the concentration and composition of the soil solution. In *Soil Sci.*, v. 12, p. 209-231.
- (7) PETERSON, P. P. 1911 Effect of heat and oxidation on the phosphorus of the soil. *Univ. Wis. Agr. Exp. Sta. Res. Bul.* 19.
- (8) SHEDD, O. M. 1920 A short test for easily soluble phosphate in soils. In *Soil Sci.*, v. 2, p. 111-122.
- (9) SHEDD, O. M. 1921 A comparison of the calcium content of some virgin and cultivated soils of Kentucky by an improved method for the estimation of this element. *Ky. Agr. Exp. Sta. Res. Bul.* 236.
- (10) SWANSON, C. O., AND MILLER, R. W. 1917 The sulfur content of some typical Kansas soils and the loss of sulfur due to cultivation. In *Soil Sci.*, v. 3, p. 139-148.
- (11) TRUOG, E. 1922 The feeding power of plants. In *Science*, v. 56, p. 294-298.
- (12) WHITSON, A. R., AND STODDART, C. W. 1909 Factors influencing the phosphate content of soils. *Wis. Agr. Exp. Sta. Res. Bul.* 2.

RECIPROCAL REPRESSION EXERTED BY CALCIC AND MAGNESIC ADDITIONS UPON THE SOLUBILITY OF NATIVE MATERIALS IN SURFACE SOIL

W. H. MACINTIRE, W. M. SHAW AND J. B. YOUNG

University of Tennessee Agricultural Experiment Station

Received for publication June 1, 1923

INTRODUCTORY

In a previous contribution (10) it was shown that basic interchange was brought about in the *subsoil* by surface soil leachings impregnated with a preponderance of either calcium or magnesium. It was also shown that an excess of solid phases of one base was *depressive* upon the *surface-soil* outgo of the other. In the earlier work, which extended over an 8-year period, seven calcic and magnesic materials were applied in excessive amounts. Each material was added in chemical equivalence at three rates, 8, 32, and 100 tons of CaO per 2,000,000 pounds of soil. The present contribution is the result of a 5-year lysimeter study with another, though similar, soil to which light additions of limestone, dolomite, CaO, and MgO were made. Both light and heavy amounts of CaO and MgO were used also in conjunction with each of three sulfur carriers, FeSO₄, pyrite, and elementary sulfur. The 8-year study was based upon an installation of both shallow and deep tanks, and certain functions of the subsoil were definitely determined. In the study here reported, however, the lysimeters contained surface soil only. In previous reports the outgo of sulfates (7) and the depressive activities of the calcic and magnesic additions upon potassium outgo (8) were reported for the same tanks. Nitrates and bicarbonates have also been determined, though not reported. This article deals with the total leachings of salts of calcium and magnesium, as such are influenced by form and amount of addition, basic repression, and both initially soluble sulfate and sulfate generated by chemical oxidation and sulfofication of the two unoxidized forms of sulfur. In the interpretation of the calcium and magnesium outgo from those tanks which received the supplements of sulfur carriers it is helpful to have available the data as to their sulfate leachings (7).

METHODS

As stated in the paper (7) on sulfate outgo, the 3750-pound addition was intended to represent a 2000-pound application of burnt lime plus 1750 pounds to care for the immediate or potential acidity of the sulfurous materials. Limestone and dolomite additions were both of 100-mesh fineness. The acid loam used contained 0.217 per cent of CaO and 0.398 per cent of MgO, as determined by Na₂O₂-Na₂CO₃ fusion. Descriptions of equipment used, analyses of treatments, and precautions followed in handling and mixing treatments throughout the body of the soil have been given, (4, 7) and will not be repeated here. The amounts of calcium and magnesium brought down in rainfall also have been reported (5), but these experimental and minor constants will be considered as inherent in the soil.

PRESENTATION AND DISCUSSION OF DATA

Annual losses of calcium, totals for the five years, and average annual increases or decreases above the control are shown for the twenty-two tanks in table 1. The magnesium data are given in similar form in table 2. Totals of calcium-magnesium salts from the control and light unsupplemented additions are presented in table 3. Since all treatments were based upon chemical equivalence, the results are reported throughout in terms of CaCO_3 . The discussion of results follows the order of treatment and grouping of tables 1, 2, and 3.

TABLE 1

Annual and total amounts of calcium salts leached from "Cherokee" loam during a 5-year period—treatments of limestone, and dolomite, and of CaO and MgO with and without additions of FeSO_4 , pyrite and powdered sulfur

TANK NUMBER	TREATMENT		Sulfur constant of 1,000 lbs. per 2,000,000 lbs. of soil	CaCO_3 EQUIVALENT PER 2,000,000 LBS. OF SOIL					Increase over no-treatment control		
	Calcic-Magnesic			Annual periods							
	Material	CaO equivalent per 2,000,000 lbs. of soil		First	Second	Third	Fourth	Fifth	Average	Total	
		lbs. or tons	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	
50	None	None	None	291	248	234	260	188	244	1,221
51	Limestone	2000	None	370	406	336	351	201	333	1,664	443
52	Dolomite	2000	None	230	273	228	219	166	223	1,116	-105
53	CaO	2000	None	406	408	278	371	226	340	1,689	468
54	CaO	3750	None	694	587	477	482	293	507	2,533	1,312
55	MgO	2000	None	155	147	166	161	111	148	740	-480
56	MgO	3750	None	147	143	166	160	96	142	712	-509
57	None	None	FeSO_4	1,348	611	374	278	173	557	2,784	1,563
58	CaO	3750	FeSO_4	2,536	718	351	338	205	830	4,148	2,927
59	MgO	3750	FeSO_4	579	139	121	101	89	206	1,029	-192
60	CaO	32 tons	FeSO_4	3,799	1,648	1,863	1,350	1,229	1,980	9,889	8,668
61	MgO	32 tons	FeSO_4	82	60	103	94	60	80	399	-822
62	None	None	Pyrite	585	896	615	381	308	557	2,785	1,564
63	CaO	3750	Pyrite	865	1,108	643	869	380	773	3,865	2,644
64	MgO	3750	Pyrite	297	242	166	159	48	182	912	-309
65	CaO	32 tons	Pyrite	4,950	1,724	1,276	1,496	1,161	2,121	10,607	9,386
66	MgO	32 tons	Pyrite	99	69	88	92	56	81	404	-817
67	None	None	Sulfur	1,279	617	400	306	186	558	2,788	1,567
68	CaO	3750	Sulfur	2,311	903	384	344	234	835	4,176	2,955
69	MgO	3750	Sulfur	526	209	245	189	119	258	1,288	67
70	CaO	32 tons	Sulfur	4,162	1,968	1,772	1,864	1,342	2,222	11,108	9,887
71	MgO	32 tons	Sulfur	55	65	90	104	59	75	373	-848
Rainfall (August to August) in inches.....			37.69	51.54	54.75	55.19	56.75	51.16	

TABLE 2

Annual and total amounts of magnesium salts leached from "Cherokee" loam during a 5-year period—treatments of limestone, and dolomite, and of CaO and MgO with and without additions of FeSO₄, pyrite and powdered sulfur

TANK NUMBER	TREATMENT		CaCO ₃ EQUIVALENT PER 2,000,000 LBS. OF SOIL									Increase over no-treatment control	
	Material	Calcic Magnesia CaO equivalent INT. 2,000 (MgO lbs. of soil	Annual periods					5-year period					
			First	Second	Third	Fourth	Fifth	Average annual	Total	lbs.			
		lbs. or tons	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	
50	None	None	174	90	103	78	85	107	535			
51	Limestone	2000	None	143	72	59	209	60	109	543	8		
52	Dolomite	2000	None	338	236	150	230	169	223	1,113	578		
53	CaO	2000	None	159	82	61	100	75	95	477	-58		
54	CaO	3750	None	139	67	42	162	74	97	484	-51		
55	MgO	2000	None	555	329	288	335	112	324	1,619	1,084		
56	MgO	3750	None	980	556	514	527	263	568	2,840	2,305		
57	None	None	FeSO ₄	474	140	106	147	62	186	929	394		
58	CaO	3750	FeSO ₄	347	96	55	113	83	139	694	159		
59	MgO	3750	FeSO ₄	3,683	534	349	348	227	1,028	5,141	4,608		
60	CaO	32 tons	FeSO ₄	100	9	33	76	57	55	275	-260		
61	MgO	32 tons	FeSO ₄	3,619	5,770	4,074	3,566	1,885	3,783	18,914	18,379		
62	None	None	Pyrite	300	202	142	184	129	191	957	422		
63	CaO	3750	Pyrite	373	119	68	118	85	153	763	228		
64	MgO	3750	Pyrite	1,140	1,033	546	518	291	706	3,528	2,993		
65	CaO	32 tons	Pyrite	96	48	17	87	28	55	276	-259		
66	MgO	32 tons	Pyrite	5,474	6,370	5,015	3,277	1,877	4,403	22,013	21,478		
67	None	None	Sulfur	523	151	112	132	82	200	1,000	465		
68	CaO	3750	Sulfur	280	99	57	112	40	118	588	53		
69	MgO	3750	Sulfur	3,340	795	340	769	213	1,091	5,457	4,922		
70	CaO	32 tons	Sulfur	86	35	26	62	45	51	254	-281		
71	MgO	32 tons	Sulfur	4,917	7,169	5,187	3,010	1,785	4,414	22,068	21,533		
<i>Rainfall (August to August) in inches.....</i>			37.69	51.54	54.75	55.19	56.75	51.16			

CALCIUM LEACHINGS FROM TWENTY-TWO TANKS

Limestone-dolomite-oxide group

The limestone addition increased the outgo of calcium for each of the five years. The 5-year total amounted to 443 pounds, or an annual average increase of 89 pounds. On the other hand, the equivalent dolomite addition

depressed the outgo of calcium below that of the control during four of the five years, the total depression amounting to 105 pounds.

Both CaO additions increased calcium concentrations in the leachings. The 1750-pound supplement to the 2000-pound addition augmented, by 844 pounds for the five years, the 468-pound increase caused by the 2000-pound addition. From previous studies with practically the same soil (3), it was determined that an application of 4000 pounds of CaO was all fixed in non-hydrate and non-carbonate forms within less than ten days. The increase in calcium leachings came, therefore, from the solvent action of acids formed biologically and by increase in bicarbonates derived through hydrolysis of the calcium silicates.

The decreased yields of calcium from the two magnesia additions were in close agreement, with striking uniformity for annual losses. The carbonate elimination, through fixation, observed with reference to CaO was known to

TABLE 3

Five-year totals of calcium-magnesium outgo from 2000-pound CaO-equivalent additions of CaO, MgO, limestone and dolomite and 3750-pound CaO and its MgO equivalent

SALTS LEACHED	LOSSES EXPRESSED AS CaCO ₃ -EQUIVALENT PER 2,000,000 POUNDS OF SOIL						
	Control	From treatments (equivalent to 2,000 lbs. CaO) of:				From 3,750-lb. CaO-equivalent treatments of:	
		CaO	MgO	Lime- stone	Dolo- mite	CaO	MgO
	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.	lbs.
Calcium.....	1,221	1,689	740	1,664	1,116	2,533	712
Magnesium.....	535	477	1,619	543	1,113	484	2,840
Total.....	1,756	2,166	2,359	2,207	2,229	3,017	3,552
Combined Ca-Mg increases in excess of outgo from control....	410	603	451	473	1,261	1,796

have taken place also in the case of MgO. The positive depressions of 480 pounds and 509 pounds below the calcium outgo from the control are in harmony with the similar findings (10) where the same repressive effect was exerted by excessive and unabsorbed amounts of MgO, and also MgCO₃ and magnesite. Still further proof of the action of both light and excessive additions will be offered in this paper in the discussion of the sulfur-supplemented MgO additions, which have continued to show the depressive effect through all five years. It will be noted that the average outgo from the two MgO tanks during the fifth year was only 55 per cent of that from the control.

FeSO₄-oxide group

The action of FeSO₄ upon native alkali-earths was apparently direct. The increase in outgo of the sulfate radical from this treatment was attributable almost entirely to its combination with calcium and magnesium. Only a small

increase in potassium outgo resulted from the treatment, as has been shown in a previous contribution (8). Lipman (2) reported the calcium and potassium content of a pressure-extraction solution obtained from lemon orchard soil, which had been treated with 5-10 pounds of commercial FeSO_4 for each tree. The FeSO_4 treatment almost doubled the soluble calcium recoverable by this method of obtaining a soil solution. The 1563-pound increase in calcium outgo is four times the corresponding increase in magnesium leachings, though the native calcium content of the soil is only about one-half that of the native magnesium. From this it is evident that the calcium complexes are much more subject to the solvent derived from FeSO_4 than are those of magnesium.

The 2000-pound supplement to the 1750-pound addition required to care in full for the sulfate radical was also drawn upon, most probably, to account for the still further increased outgo from tank 58. The 4148-pound total from this tank, 2536 pounds of which came out during the first year, is 2927 pounds in excess of the loss from the control and 1364 pounds more than the increased loss of native calcium from the unsupplemented FeSO_4 addition. The sudden drop from the maximum of the initial year, and the progressive decreases during the last four years, mark the removal of a major portion of the calcium sulfate and the advent of a large proportion of calcium bicarbonate. This outgo in calcium harmonizes with the periodicity of sulfate leachings which have been reported (7).

The calcium leachings from the 3750-pound MgO-FeSO_4 treatment during the first year amounted to more than one-half of the 5-year total. The influence of magnesium sulfate derived from the MgO-FeSO_4 additions is evidenced during this period. Most of the added sulfate having passed out during the first year, the residue of the magnesia addition exerted thereafter a depressive influence upon calcium outgo, which amounted to only 450 pounds, as against 930 pounds from the control for the last four years. The balance between the 288-pound increase of the first year and the 480-pound cumulative depression of the last four years amounted to 192 pounds. In other words, in spite of the magnesium-calcium interchange brought about by magnesium sulfate during the period before its removal by leaching, the magnesia addition still demonstrated a conservation of the native stores of calcium.

The greatest yield of calcium from the 32-ton CaO treatment used in conjunction with the ferrous sulfate came during the first year. With varying proportions this yield was accounted for by hydroxide, sulfate, nitrate, carbonate, and bicarbonate of calcium. After the first year the outgo decreased progressively. Of the total increase of 8668 pounds above the control for the 5-year period, an increase of 3508 pounds, or 40 per cent, is accredited to the first year. But this 40 per cent outgo of added CaO carried only 82.2 pounds of the 1000 pounds of sulfur added in the soluble sulfate form (7).

Applied with FeSO_4 , the 32-ton MgO addition gives a still more striking depressive influence upon calcium-salt outgo. The excess of MgO entirely nullified the liberative or replacement activity which was apparently exerted by

the magnesium sulfate derived from the lighter MgO addition with FeSO₄. During each of the five years the calcium outgo was but a fractional part of that from the no-treatment control, and a still smaller fraction of that from the sulfate control. The 5-year total of 399 pounds from tank 61 falls 822 pounds short of equalling that from the no-treatment tank 50, and 2385 pounds below that of tank 57, the FeSO₄ control.

The pyrite-oxide group

The order of annual losses of calcium from the pyrite control differed from that of the FeSO₄ control. The unsupplemented pyrite increased the 291-pound loss from the no-treatment control to 585 pounds, during the first year, as against 1348 pounds for the sulfate control. The oxidation of the pyrite apparently was most extensive during the second year, as indicated by the maximum calcium yield, and also by the maximum sulfate leaching during that year (7). The total calcium increase caused by the pyrite during the 5-year period was practically identical, however, with that caused (7) by ferrous sulfate and by elementary sulfur, though the pyrite addition gave the minimum sulfate recovery of the three materials during that time. These three CaCO₃-equivalent totals were, respectively, 1564, 1563, and 1567 pounds per 2,000,000 pounds of soil. But when added with pyrite, the light lime treatment enhanced the total calcium outgo by only 2644 pounds, or 293 pounds less than when used with ferrous sulfate and 311 pounds less than when used with elementary sulfur. This disparity is accounted for by the fact that the oxidation of the pyrite addition was less rapid and less in the aggregate than that of the elementary sulfur (7), for the sulfur recoveries from the FeSO₄ and elementary sulfur were both over 90 per cent of the additions, after deduction of the 5-year rainfall sulfur, while the pyrite gave a corresponding recovery of only 60 per cent.

When added with pyrite, the light MgO addition exhibited, after the second year, a depressive effect similar to that shown by the same oxide when used with ferrous sulfate. The largest leachings of both calcium and sulfates occurred during the first two years. Because the oxidation of pyrite was less rapid in the pyrite-MgO tank than in the pyrite control (7), less of magnesium sulfate was at hand to offset the depressive action of the MgO treatment. Hence, the depressive action of the light MgO addition was considerably greater when used with pyrite than when used with ferrous sulfate. It will be noted that after the 6-pound increase of the first year the treatment showed progressive annual depressions of 6, 68, 101, and 104 pounds below corresponding no-treatment yields.

The maximum outgo from the pyrite and 32-ton CaO addition came during the first year, with a tendency toward progressive decrease thereafter. During the early period, as parallel with persistence of the hydrate, the outgo of lime was almost entirely in forms other than sulfate, a total sulfate sulfur recovery of only 31.5 pounds having been obtained from the 1000-pound addition (7).

The excess of CaO was either depressive to both chemical oxidation and sulfification, or inactive toward one or both of these processes, yet depressive upon sulfate removal by leaching, if sulfates were formed. For, as has been previously pointed out (7), not only was the excess of CaO depressive to the outgo of sulfates from pyrite, but during the persistence of hydrate it also inhibited the outgo of the added sulfate of iron, since only 82.2 pounds of the 1000-pound addition of sulfate sulfur was leached during the first year.

Applied with pyrite, the 32-ton MgO addition again proved distinctly depressive upon the outgo of native calcium during each of the five years. Even had $MgSO_4$ been present as a liberating salt, the excess of MgO was such as to nullify any tendency to effect basic exchange. This was shown in the case of the 32-ton MgO and $FeSO_4$ treatment. Differing, however, from the elementary sulfur and heavy MgO combinations, where the MgO proved accelerative to the formation of sulfates, the same addition of MgO exerted the opposite effect upon the pyrite. The total depression in calcium outgo amounted to 817 pounds. This is in remarkable agreement with the 5-year totals of 822 pounds and 848 pounds for the same oxide and rate when used in conjunction with ferrous sulfate and elementary sulfur, respectively.

Sulfur-oxide group

The sulfur addition increased the concentration of calcium salts in the leachings from the control during each of the first four years, particularly during the first year. Both calcium outgo and sulfate recoveries (7) progressively decreased during the 5-year period. Total outgo, as has been previously mentioned, is very close to losses from the other two sulfur-carrier controls.

The light CaO addition accelerated conversion of the elementary sulfur into sulfates, as was demonstrated by the increase in sulfate leachings (7). A large part of the 2020-pound increase over the calcium outgo from the untreated tank during the first year is accounted for in this way, since 733.5 pounds of sulfate sulfur came from the combination of light lime and sulfur during the first year, as against 506.8 pounds from the unsupplemented sulfur control. The rate of outgo of calcium decreased progressively during the five years. The same was true also of sulfate leachings. Of the total 3750-pound CaO addition, including the 1750-pound portion intended to care for potential acidity, 2955 pounds were leached. That is, the excess above the outgo from the control represented the 1750-pound neutralizing addition plus 1205 pounds, or 60 per cent, of the 2000 pounds intended as the soil-ameliorant treatment.

In agreement with the corresponding MgO addition in the ferrous sulfate group, the lighter MgO produced an increased outgo of calcium during the first year, during which period 816.6 pounds of sulfate sulfur (7) was removed by leaching. The calcium liberation was apparently caused by the activity of engendered magnesium sulfate. Depressive influence of MgO in the MgO-sulfur combination was evidenced after the third year, when the effect of the generated sulfate had been eliminated because of its removal. The liberation

of calcium by the engendered magnesium sulfate during the first year was more than sufficient to offset the depression in calcium outgo during the latter period. As a result, there was a gain of 67 pounds over the no-treatment control during the 5-year period. Comparing the yield from tank 69 with the findings from tanks 64 and 59, it appears that with intensive initial and progressively decreasing generations of magnesium sulfate the depressive action of MgO was nullified for the 5-year period; that with slower and more irregular oxidation of pyrite and a resultant minimum of magnesium sulfate occurrence, the most depressive influence exerted by the light MgO addition was of effect; and, with the maximum amount of magnesium sulfate formed and leached during the first year, the intermediate depressive activity was in evidence.

The maximum calcium outgo from the heavy CaO and sulfur addition came during the first year. Only a small part of this early outgo could be accounted for by the 88 pounds of added sulfur which was leached out in the sulfate combination. During the persistence of considerable quantities of $\text{Ca}(\text{OH})_2$ from the CaO addition, sulfification was most probably inhibited or greatly depressed. Even had sulfification taken place, however, the CaO- FeSO_4 parallel demonstrated that sulfates so generated would not have been leached (7).

Incorporated in the soil along with sulfur, the heavy MgO addition again shows a result which corresponds to that obtained when it was used in conjunction with both ferrous sulfate and pyrite. It has been shown (7) that, when admixed with 32 tons of MgO, the elementary sulfur was rapidly converted into sulfates. But the resultant excess of magnesium sulfate induced no magnesium-calcium interchange when in contact with the large excess of unabsorbed MgO. This result is also in agreement with that obtained when the soluble sulfate was added along with the heavy addition of MgO. The uniformity of calcium outgo from the heavy treatment of MgO may be stressed by repetition of the comparison between tanks 71, 66, and 61. The disparities below the outgo from the no-treatment control demonstrated repressions in the solubility of native calcium, as represented by depressions in calcium outgo of 848, 817, and 822 pounds, respectively.

MAGNESIUM LEACHINGS FROM 22 TANKS

Limestone-dolomite-oxide group

The 100-mesh limestone depressed the outgo of magnesium during four of the five years. The accelerative influence indicated during the fourth year was sufficient, however, to offset the cumulative differences which resulted from the reverse action during the other four years. Many of the losses for the fourth year indicated that the periodicity of rainfall during that period caused abnormality in the leaching of soluble salts.

Magnesium outgo from the dolomite addition was consistently higher than from the control. As a result, the magnesium increase for the 5-year period was slightly more than 100 per cent of the loss from the no-treatment tank.

Again, as in the case of the limestone additions, the economic additions of CaO caused a decreased magnesium outgo during four of the five years; but the abnormality of the fourth year served to neutralize, in part, the cumulative results of the other four years. Hence, the two CaO treatments showed magnesium depression totals of but 58 pounds and 51 pounds.

Both MgO additions showed a substantial influence upon magnesium outgo. The 3750-pound treatment gave results consistently higher than those from the 2000-pound application. Were it not for the abnormality in leachings common to the six tanks 51-56 during the fourth year, both MgO additions would have shown maximum outgo during the first year, with progressive decreases during the succeeding four years. The increase from the 2000-pound addition was 54 per cent of the amount added, while that from 3750 pounds of MgO was 61 per cent of the addition.

FeSO₄-oxide group

The solvent action of the unsupplemented FeSO₄ treatment was most marked during the first year. Over one-half of the added sulfate was recovered during that period. The 394-pound gain in the magnesium leachings of the first year represented an increase of 73.6 per cent over the outgo from the no-treatment control.

The light CaO supplement to the FeSO₄ treatment caused the formation of CaSO₄, and this salt apparently effected an interchange with native magnesium. After the removal of the CaSO₄ and MgSO₄ so accounted for, the residual effect of the CaO was more repressive than augmentive. As a result of such direct solvent action and interchange, the supplemented ferrous sulfate induced a 5-year increase of only 159 pounds in magnesium outgo, as against 392 pounds where the FeSO₄ was not subjected to the intervening influence of the CaO supplement.

Of the total increase of 4608 pounds from the 3750-pound MgO addition with FeSO₄, 3509 pounds, or 73.6 per cent, was leached during the first year, after which period there was a tendency toward progressive decrease to the minimum outgo of the fifth year. The total outgo of 5141 pounds represented a gain of 4608 pounds, or 858 pounds more than the addition. Thus, from an addition of MgO in connection with FeSO₄, solvent action of the soluble salt plus biological activation has resulted in a large supplemental loss of the native magnesium.

The heavy addition of CaO exerted a decidedly depressive tendency upon the yield of native magnesium to the free soil water. The large excess of the oxide nullified the liberative tendency of 4246 pounds of calcium sulfate formed by reaction between Ca(OH)₂ and the soluble iron sulfate. The magnesium outgo was consequently decreased to about one-half of that from the no-treatment control. Contrasted with the enhanced outgo from the FeSO₄ control, this decreased outgo gives a differential of 654 pounds, as representing the extent of the repressive action of the excess of calcium oxide.

The 32-ton MgO addition was more than sufficient to saturate the soil by exceeding its capacity to absorb, or "silicate," the added oxide. A large excess of MgO was therefore available for carbonation and leaching as bicarbonate by direct reaction of available H_2CO_3 , whereas hydrolysis of the completely absorbed 3750-pound addition was essential to its removal in the bicarbonate form. Nitrate and sulfate generations were also accelerated by the heavy addition. As a result, an increased magnesium outgo of 18,379 pounds was obtained.

Pyrite-oxide group

Oxidation of the pyrite-control treatment was sufficiently rapid to cause an appreciable increase in outgo of magnesium for each of the five years. The total increase for the 5-year period was almost equal to the outgo from the control. After the maximum of the first year, the annual losses showed tendency toward progressive decrease.

Subsequent to the first year, there was little evidence of magnesium liberation from the light addition of CaO. Of the total increase of 228 pounds over the pyrite control, 199 pounds came during the first year, and should be considered most probably as a sequence of pyrite oxidation and either direct solvent action or interchange resulting from the maximum occurrence of soluble calcium salts.

With depressed pyrite oxidation, caused by the MgO addition, the outgo of magnesium from the light addition showed a gain of but 2993 pounds for the 5-year period, as against the larger increases of 4608 pounds for the sulfate addition and 4922 pounds for the rapidly oxidized sulfur. The annual losses from the light MgO decreased yearly after the maximum of the first year.

In the case of the heavy lime tank 65, there was a very positive depression in magnesium outgo. As previously shown by lysimeter-leaching data (7), there was a minimum of calcium sulfate in the solution phase to effect basic replacement. If the total pyrite addition had been oxidized 4246 pounds of calcium sulfate would have been present. Its tendency toward magnesium liberation would, however, have been nullified by the excess of CaO, as is shown by the practically identical depression in outgo, 259 pounds, or a decrease of 276 pounds below the 535-pound outgo from the no-treatment control caused by the same calcic treatment when used in connection with the soluble sulfate.

It has been pointed out (7) that the 32-ton MgO addition was decidedly depressive upon the oxidation of pyrite. Consequently, in this instance, less of magnesium sulfate was present to function as a calcium liberant. As would be expected, a large amount of magnesium bicarbonate was leached following the conversion of the excess of oxide to carbonate. It was noted previously in this contribution that the effect of the excessive outgo of magnesium bicarbonate, or that of the excess of residual $MgO \cdot Mg(OH)_2 \cdot MgCO_3$, was to decrease materially the outgo of calcium salts derived from native calcic materials.

Sulfur-oxide group

In agreement with the FeSO_4 and pyrite controls, the unsupplemented sulfur addition gave a material increase in magnesium outgo. This increase may be charged to the rapid oxidation of the elementary sulfur, as was shown in previously reported (7) sulfate-outgo results.

The light CaO treatment resulted in a distinct acceleration of the oxidation of the added sulfur and in the formation of calcium sulfate. This increase is reflected in the failure of the light lime addition to show a depressing effect upon magnesium outgo. The smaller increase of 53 pounds, as compared with the 159-pound and 228-pound increases from the FeSO_4 and pyrite parallels, may be accounted for by the fact that the light addition of lime with sulfur gave a rapidity of sulfate outgo which was intermediate between the other two. The sulfate radical from the sulfur with light lime was most probably generated at a speed which caused it to react primarily with the calcium oxide, and in small measure with native magnesic complexes. The entire amount of oxidized sulfur may, however, have combined with the added calcium, in which case the resultant calcium sulfate—4246 pounds—would have effected basic interchange in the absence of added lime in sufficient excess to be depressive to magnesium outgo.

The light MgO proved even more accelerative to sulfification, and, as is known from unpublished data, to nitrification also. The 4922-pound excess of magnesium outgo over the control, represents the 3750-pound addition plus 1172 pounds of magnesium native to the soil. The enhanced outgo of 4922 pounds of CaCO_3 equivalence calculates to 5906 pounds of MgSO_4 which would account for 1574 pounds of sulfur. The total 5-year outgo of sulfate sulfur from this tank was, however, only 1136 pounds (7), of which 257 pounds was accounted for by rainfall. The 1172-pound excess above the control outgo and 3750-pound addition was attributable therefore not only to enhanced sulfification, nitrification, and CO_2 generation, as the products of these activities may have been neutralized by the MgO addition, but also through the combined influence of the same activities upon non-carbonate magnesic material native to the acid soil. In other words, the light magnesia addition not only suffered complete removal, but it so stimulated soil activities as to cause a further outgo of native magnesium.

In agreement with the corresponding heavy lime additions of tanks 60 and 65, and with previously reported data (10) upon the same treatment at the same rate without sulfur, the 32-ton addition of tank 70 has proved depressive to the leaching of magnesium for each year, the total depression for the 5-year period amounting to 281 pounds. Agreeing also with previous findings (6, 7), carbonation of $\text{Ca}(\text{OH})_2$ was precedent to accelerated outgo of sulfates.

The 5-year total outgo from the 32-ton MgO treatment was practically the same as that from the same treatment when it was used in conjunction with pyrite. In the case of the sulfur supplement, both speed and aggregate of

sulfate outgo were much greater than in the case of the MgO-pyrite combination. A larger proportion of magnesium sulfate and a smaller proportion of bicarbonate is therefore accredited to the sulfur plus heavy MgO, since the determined difference in nitrate leachings was insufficient to be considered as a factor in this connection. On the other hand, practically all of the applied soluble sulfate was removed by the heavy MgO addition during the first year. The smaller total of 18,379 pounds may be accounted for by the probability that the sulfate addition was depressive, initially, at least, to the generation of CO₂, which depression caused a lesser outgo of magnesium bicarbonate.

CALCIUM-MAGNESIUM TOTALS LEACHED FROM THE LIMESTONE-DOLOMITE-OXIDE GROUP

The most common application of ground limestone is two tons per acre every four or five years, while burnt lime is generally applied at the 1-ton rate. Very few data are available as indicative of the calcium-magnesium losses from the *surface zone*, where many plants feed most extensively. The foregoing discussion shows that the problem of liming is a dual one of calcium-magnesium conservation. Total calcium-magnesium results from the most generally used economic applications and the 3750-pound addition, as approximating the 2-ton CaO addition, which is often made, are of particular interest. It will be remembered that for a given rate, all treatments in this experiment were of constant chemical equivalence.

At the 1-ton oxide-equivalence rate, all treatments gave combined alkali-earth losses in excess of those from the control; but the proportions of calcium to magnesium in the totals varied widely. It should be stressed that from much parallel work with the same type of soil and the same additions, it is known that all of the added calcic and magnesian treatments were quickly fixed as non-carbonate forms by this soil. The leachings were therefore derived from the reversal of the absorption processes, as a result of the action of carbonated water of the soil upon the calcium-silica complexes, except where biologically engendered acids may have acted directly upon the alkali-earth silicates. With this thought in mind, we observe that the 410-pound increase from burnt lime is due entirely to enhanced calcium outgo, since the magnesium leachings were less than those of the control. In a similar manner, it appears that the 451-pound increase accredited to the limestone is also due solely to calcium, since the magnesium leachings were within 8 pounds of those from the control. On the other hand, there came from the MgO addition a 603-pound excess over the total outgo from the control, which excess is attributable entirely to augmented outgo of magnesium, for the 750-pound calcium outgo is 481 pounds less than that from the control. Likewise, we find that the dolomite gave an increase which is attributable solely to magnesium. However, the dolomite addition proved less repressive than MgO upon calcium outgo. This may be due to the formation of a dual salt when the calcium and magnesium of the dolomite are absorbed by the soil. The dolomite contains the two

elements in nearly equivalent amounts, as contrasted to the mass of magnesium and near-absence of calcium in the case of the MgO addition.

When applied at the 3750-pound rate, both oxides gave total calcium-magnesium yields in excess of the near-constants from the four materials at the 2000-pound rate. The MgO showed a more rapid and greater total leaching, as it did also at the 2000-pound rate and as it has done for all rates with this and a similar soil (10). The full increase of 1261 pounds from the 3750 pounds of CaO is due entirely to increased CaO from the addition, for the magnesium outgo was depressed below that of the control. Conversely, the outgo of magnesium from the corresponding magnesia addition accounted in full for the increase of 1796 pounds in total outgo because the calcium leachings were depressed 509 pounds by the 3750 pounds of MgO.

From these data it is evident that equivalent and well-disseminated amounts of CaO, limestone, and dolomite at the 2000-pound-equivalent rate were responsible for practically identical amounts of total calcium-magnesium salts. The ratio of the leached bases varied, however, with consequent change in ratio of residuals and possibly also their availability. The imposed conditions differ from those of the excessive carbonate additions, considered in a previous contribution (10), where the unabsorbed excesses were such that the gaseous phase carbon dioxide was the limiting factor. In the present case the treatment was so limited as to insure complete absorption by the soil, and the dispersion throughout the mass was so thorough that the bulk of the addition and its absorption products represent the controlling factor. Assuming equivalent quantities of CO₂ for the 2000-pound and 3750-pound additions of CaO and MgO—though the heavy treatment may have been more potent in generating carbon dioxide—it appears that the larger addition insured so much wider and more uniform distribution that the available carbon dioxide had a better chance to function in the formation and leaching of bicarbonates.

Another point is suggested relative to the conservation of calcium and magnesium. The CaO, limestone, and dolomite additions of chemical equivalence show 5-year calcium-magnesium losses of about one-fifth of the respective incorporated materials. Were this rate of outgo to continue, the additions would require at least twenty-five years for their dissipation. But, since the increases over the control calcium-magnesium total are progressively decreasing, it is probable that a much larger period would be required for the removal of the additions through leaching. In practice, however, we find that a 2000-pound CaO-equivalent addition should be repeated every four, five or six years, depending upon soil type, composition, method of handling, cropping, topography, and rainfall. With the large part, nearly four-fifths, of the added materials still present in this case, it appears that as the time increases, the absorbed materials become more complex, less soluble, and more nearly corresponding to the availability of the long-aged natural non-carbonate alkali-earth occurrences native to the soil. In other words, the residuals of additions are subject to dynamic conditions and to aging, through which process

they become more and more insoluble and unavailable, and hence of lessened ability to maintain conditions of fertility.

Applying the findings to this particular soil, the response of which to liming under field conditions is known, infertility would be eliminated by the liming material during some rather immediate period after its incorporation in the soil. Recurrence of what would be, in effect, lime poverty would follow because the aging of the absorbed residual from the addition. As corollary evidence derived from the same type of soil the aging of an excess of magnesium has caused transition of toxicity into fertility (9). In this latter case an 8-ton CaO-equivalent of $MgCO_3$ was found to be lethal to tall oat grass several months after the carbonate had been completely fixed or silicated in the soil. About one year later, however, the non-carbonate residual proved beneficial, rather than toxic, though most of added magnesium was still present.

An additional practical application follows from the results, in so far as other similar soils may react with economic amounts of calcic and magnesic materials. Where a crop has a need for magnesium, that earthy alkali should be applied. For such a need will not be cared for through basic interchange in the surface soil, following additions of high-calcic materials. Rather, a decrease in magnesium solubility follows. In a similar manner magnesium additions tend to decrease the solubility of native calcic materials in the soil. Both limestone and dolomite exert some depression, but they are relatively inactive in this regard, as compared, respectively, with burnt lime and burnt magnesia. A later report of work now under way for over two years will give further data relative to the activity of burnt dolomite in this respect. It is quite probable that the results here reported will materially aid in the practical usage of calcareous and dolomitic products used with tobacco and similar crops, which may be subject to chlorotic magnesium deficiency, described by Garner and others (1).

SUMMARY

Leaching data from twenty-two lysimeters over a 5-year period are reported. Limestone, dolomite, CaO, and MgO unsupplemented were added in equivalence to 2000 pounds of CaO per 2,000,000 pounds of soil. Both CaO and MgO were also used unsupplemented at the rate of 3750 pounds. At the same rate and also at 32-ton rate, the two oxides were used with a 1000-pound constant of sulfur added as $FeSO_4$, pyrite and elementary sulfur. Many points as to periodicity of leachings are included in the text, but totals only will be stressed in the summary.

The completely absorbed limestone addition increased the calcium outgo and had no positive effect upon magnesium leachings, while the dolomite addition decreased the calcium outgo and increased magnesium leaching.

Both CaO additions increased outgo of calcium and depressed that of magnesium.

Both MgO additions depressed decidedly the outgo of calcium, while increasing that of magnesium.

FeSO_4 , unsupplemented, increased the loss of native calcium and magnesium. When supplemented with the light CaO addition, it doubled the increase in outgo of calcium. The CaO supplement depressed the solvent action of the FeSO_4 upon native magnesium. Although increasing magnesium outgo, the light MgO addition was repressive to the solubility of native calcium. The heavy CaO supplement to FeSO_4 increased the calcium outgo and depressed that of magnesium to a point below the outgo from the control. Conversely, the heavy MgO supplement nullified the replacement tendency of MgSO_4 and depressed the outgo of calcium by 822 pounds.

The unsupplemented pyrite acted as did FeSO_4 upon native calcium and magnesium. The light CaO also acted as it did when used as a supplement to FeSO_4 , by accelerating calcium outgo and repressing the liberative tendency of the engendered CaSO_4 . Conversely, light MgO , with pyrite, served to depress calcium outgo below that of the control, while increasing magnesium leachings. The heavy addition of CaO gave enhanced yields of calcium, but positive depressions of native magnesium outgo. In similar manner the heavy MgO supplement, with pyrite, was responsible for a marked decrease in calcium outgo, along with enhanced losses of magnesium.

Sulfur alone caused increased losses of both calcium and magnesium, the losses agreeing closely with those from the FeSO_4 and pyrite controls. The leachings from the light addition of lime with sulfur contained still more of calcium and less of magnesium. The light addition of MgO increased magnesium losses and almost nullified the liberative activity of the MgSO_4 formed by the accelerative action of magnesia upon the oxidation of the sulfur addition. The heavy lime treatment acted as it did with the other two sulfur carriers by increasing calcium losses and depressing magnesium outgo. Again, the heavy MgO supplement, with sulfur, exhibited a distinctly retardative effect upon calcium outgo, while increasing the leaching of magnesium.

The 2000-pound-equivalent additions of CaO , limestone, and dolomite gave near-equal calcium-magnesium totals. The increases from these treatments amounted to only about one-fifth of the amounts added. The increases from CaO and limestone were due entirely to calcium, while those from dolomite and MgO , were due to enhanced losses of magnesium, the calcium outgo having been less than that of the control. The 3750-pound additions of CaO and MgO proved augmentive to totals, but reciprocally depressive upon outgo of native materials.

The losses of about one-fifth of the total unsupplemented additions at the 2000-pound rate, and the progressively decreasing leachings, indicate that after absorption the added calcium and magnesium undergo aging and consequent decrease in solubility and availability. Such a result would be anticipated only where silicate complexes occur in considerable proportions.

Possible practical applications of the findings are mentioned.

REFERENCES

- (1) GARNER, W. W., McMURTRY, J. E., BACON, C. W., AND MOSS, E. G. 1923 Sand down, a chlorosis of tobacco due to magnesium deficiency, and the relation of sulphates and chlorids of potassium to the disease. *In Jour. Agr. Res.*, v. 23, no. 1, p. 27-40.
- (2) LIPMAN, C. B. 1922 Ferrous sulfate treatment of soil as influencing the soil solution obtained by the Lipman pressure method. *In Soil Sci.*, v. 13, p. 55-56.
- (3) MACINTIRE, W. H. 1919 The carbonation of burnt lime in soils. *In Soil Sci.*, v. 7, p. 325-453.
- (4) MACINTIRE, W. H. 1919 The liberation of native soil potassium induced by different calcic and magnesic materials, as measured by lysimeter leachings. *In Soil Sci.*, v. 8, p. 337-395.
- (5) MACINTIRE, W. H., AND YOUNG, J. B. 1923 Sulfur, calcium, magnesium and potassium content and reaction of rainfall at different points in Tennessee. *In Soil Sci.*, v. 15, p. 205-227.
- (6) MACINTIRE, W. H., SHAW, W. M., AND YOUNG, J. B. 1923 The influence of calcic and magnesic additions upon the outgo of sulfates from a loam soil as measured by lysimeter leachings over an 8-year period. *In Soil Sci.*, v. 16, p. 1-40.
- (7) MACINTIRE, W. H., SHAW, W. M., AND YOUNG, J. B. 1923 Influence of calcic and magnesic additions upon the leaching of sulfates from native soil alone and with additions of ferrous sulfate, pyrite, and sulfur. *In Soil Sci.*, v. 16, p. 159-182.
- (8) MACINTIRE, W. H., SHAW, W. M., AND YOUNG, J. B. 1923 A 5-year lysimeter study of the supposed liberation of soil potassium by calcic and magnesic additions. *In Soil Sci.*, v. 16, p. 217-223.
- (9) MACINTIRE, W. H., AND YOUNG, J. B. 1923 The transient nature of magnesium-induced toxicity and its bearing upon lime-magnesia ratio studies. *In Soil Sci.*, v. 15, p. 427-471.
- (10) MACINTIRE, W. H., SHAW, W. M., AND YOUNG, J. B. 1923 The variant rôles of soil and subsoil in calcium-magnesium interchange. *In Soil Sci.*, v. 16, p. 321-341.

COMPARISON OF THE SOIL SOLUTION BY DISPLACEMENT METHOD AND THE WATER EXTRACT OF ALKALI SOILS

P. L. HIBBARD

University of California, Agricultural Experiment Station

Received for publication October 1, 1923

For the purpose of this discussion, the expression "soil solution" means the watery solution obtained from moist soil by the displacement method as described by Burd and Martin (1, 2). The water extract of the same soils was made at the same time from another portion of the same homogeneous mass of soil by mixing with five times its weight of distilled water nearly free from CO₂ and filtering through Pasteur filters. The procedure was essentially that of the United States Bureau of Soils (4, p. 10).

DESCRIPTION OF THE SOILS USED

Soils 18, 19, 20 and K are fine sandy loams from Kearney Vineyard near Fresno. They are very similar physically. Chemically, they differ in amounts of alkalinity and salinity. Soil 18 is highly saline, not alkaline. The others are somewhat alkaline and highly saline, except K, which is the same soil as 19 after most of the easily soluble matter had been removed by flooding and leaching in the field. Soil Imperial is a fine sediment containing considerable CaCO₃. It is a composite of samples from Imperial Valley. Soil R is somewhat similar to Imperial physically and contains some CaCO₃, but is probably residual. It is found near Riverside. Soil Colusa is a composite of samples of Willows adobe clay, obtained near Cortona. Soil S1 is a sedimentary clay loam from Sutter Basin. Soil S2 is similar to S1, from the same locality, but contains less salts and more alkalinity. It is very much deflocculated, hence the solutions from it are obtained with great difficulty.

METHOD OF OBTAINING THE DISPLACED SOLUTION

The soil, previously moistened to about optimum for plant growth, is packed tightly into a brass tube three inches in diameter, seventeen inches long. The lower end is closed by a screw cap which supports a wire gauze and filter paper on which the soil rests. After the soil is packed into the tube, about 500 cc. of water are placed on top of the soil and the tube is screwed into the pressure apparatus. When it has stood thus a few hours to permit the water to diffuse into the upper soil, air pressure is applied to force the solution out at the lower end of the tube. The percolate is collected in aliquots of 5-25 cc. The electrical conductivity of each portion is determined. This is nearly constant so long as the solution is not mixed with the displacing water. A considerable change in conductivity is evidence that the true soil solution is no longer being obtained. All the like portions of solutions are united to make the solution that is to be analyzed.

The analytical methods employed were those commonly used and known to give accurate results. All quantities were found by actual determination, none

by difference. Few determinations were duplicated, but the accuracy was checked by the "reaction values".

In most cases, the error of analysis was well below 5 per cent. On account of having available only very small volumes of some of the solutions, it was not possible to repeat analytical work, and considerable percentage error is to be expected in determination of such small amounts as are involved in some of these cases.

The method of calculating and using "reaction values" is given by Chase Palmer (3). By this means, the reacting power, or combining capacity, of each ion in the solution is given a numerical representation, expressed as percentage of the reacting power of all the ions in the solution taken as 100 per cent. This permits giving the chief properties and general character of the water numerical representation so that one is readily compared with another by actual figures.

THE RESULTS OF THE ANALYSES

The figures in table 1 express the results in parts per million. In line A are given the amounts found in the 1:5 water extract as parts per million of the oven-dry soil. In line B shows the amounts given in line A as parts per million of the water which the soil contained at the time it was weighed out for analysis. In line C are given the amounts found in the displaced solution. Now if there were no interfering factors, the quantities in lines B and C should be substantially alike. But in many respects, they are unlike, so that it appears that the water extract does not truly represent the soil solution. A brief consideration of the results will bring out the differences and relationships.

Calcium. There seems to be no apparent relation between the amounts of calcium found by the two methods, as exhibited in lines B and C. It might be expected that in a nearly neutral soil they would be similar, while in an alkaline soil more calcium would be found in the water extract than in the displaced solution because of the greater dilution. The figures obtained do not support this view. The amounts of calcium found in soils 18, K, Imperial, R, S1 and S2 are somewhat similar in B and C, yet some are alkaline, some nearly neutral. For soils 19, Colusa and 20, the displaced solutions contained much more calcium than the water extracts.

Magnesium relations are equally inexplicable. No law is apparent.

Sodium. With the exception of soil Colusa, sodium found in the water extract is two to four times as much as in the displaced solution. This is probably due to hydrolysis of easily decomposed silicates in the presence of the larger proportion of water used for the water extract.

Potassium. Except in soils S1 and S2, potassium is much less in the displaced solution than in the water extract. It acts like sodium. The exception in case of S1 and S2 is seemingly unimportant, since the amounts found are almost within the limits of experimental error. The fact that more water

dissolves more potassium is of interest in plant nutrition, as indicating that more of this element may be made available by suitable soil treatment.

Carbonate. This ion is evidently dissolved in proportion to the amount of water used, since the water extract contains much more than the soil solution. The small amounts shown in line C for soils 19, K, Imperial, Colusa and S1, may be due to the solubility of CaCO_3 in the relatively greater concentration of sodium salts in the displaced solution. The water extract is likely to give a very erroneous idea of the concentration of carbonate in the actual soil solution.

Bicarbonate. This ion is misrepresented by the water extract even more than the carbonate ion. The actual soil solution is much better for plants than would appear from examination of the water extract. Bicarbonates are relatively insoluble.

Sulfate. Two or more times as much sulfate is found in the water extracts as in the displaced solution.

Chloride is more nearly similar in the two solutions, though somewhat lower in the displaced solution.

Nitrate is also much alike in both. The apparent exceptions are probably due to imperfections in analytical work, and unrepresentative character of the solutions analyzed.

Phosphate appears to form a saturated solution in all cases, so that the amount found by analysis depends on the amount of water used in making the solution. The amounts found were within the limits of analytical error in some cases, so that it is not certain that there was any phosphate at all in some solutions.

ACTUAL CONCENTRATIONS IN THE DISPLACED SOLUTIONS

To one who is in the habit of considering the amounts found by the water extraction method calculated to the weight of dry soil, the concentration of solutes in the displaced solution may appear very great. Yet this latter is essentially the solution from which plants must draw their mineral nutriment. When one realizes the osmotic pressure and the possibly caustic or corrosive character of the displaced solution from some of these saline or alkaline soils, it is much more apparent why such soils are a very unsuitable medium for support of plant life.

GEOCHEMICAL CLASSIFICATION OF THE SOLUTIONS

A cursory examination of the analytical results shows that there is a larger proportion of the salts of calcium and magnesium in the soil solution than in the water extract. But when the solutions are classified according to the system proposed by Palmer (3) their relations and differences become much more evident (see table 2). According to this system, non-hydrolyzed salts produce salinity, hydrolysable salts cause alkalinity of water solutions. In either case, sodium and potassium give primary salts, calcium and magnesium

TABLE I
Solutions in alkali soils

SOIL NUMBER	MONSTER	C _a	Mg	Na	K	CO ₃		SO ₄		Cl		NO ₃		PO ₄	
						p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.	p.p.m.
A	18	16.2	351	130	1,426	86	0	222	739	1,193	2,165	10			
B		2,160	802	8,798	529	0	1,375	4,550	7,313	13,358	62				
C		2,770	972	5,350	248	0	427	2,152	6,600	13,200	3				
A	19	12.8	10	934	47	0	493	717	705	183	22				
B		94	78	7,294	367	0	3,850	5,580	5,520	1,430	172				
C		740	238	4,614	178	24	1,520	4,403	4,850	1,116	4				
A	20	12.8	24	1,695	81	106	336	680	1,600	683	34				
B		188	31	13,250	683	827	2,650	5,310	12,500	5,340	265				
C		510	146	10,050	530	85	830	3,839	11,370	4,452	9				
A	K	11.7	104	12	216	23	0	225	602	35	21	8			
B		889	102	1,845	196	0	1,920	5,152	298	179	68				
C		700	79	998	68	Tr	622	3,222	30	87	0				
A	Imperial	20.5	65	21	582	39	0	314	844	236	269	4			
B		317	103	2,840	190	0	1,522	4,118	1,150	1,020	19				
C		530	160	940	64	Tr	158	2,304	850	223	2				
A	R	16.1	37	81	4,220	470	246	255	4,278	3,260	835	3			
B		220	502	26,400	2,940	1,525	1,585	26,500	20,300	5,170	19				
C		225	702	20,525	2,110	183	561	21,644	17,500	4,191	5				
A	Colusa	25.5	261	130	115	85	0	507	4,660	522	35	4			
B		1,023	509	450	333	0	1,980	18,267	2,050	137	16				
C		470	365	2,750	21	49	244	6,090	1,570	2					

<i>A</i>	S1	23.8	259	172	669	25	0	126	651	1,365	104	2
<i>B</i>			1,035	722	2,820	105	0	530	2,740	5,720	437	8
<i>C</i>			1,410	852	1,230	170	Tr.	244	2,035	5,265	?	2
<i>A</i>	S2	19.7	13	12	533	22	78	905	174	129	40	19
<i>B</i>			66	61	2,970	111	395	4,580	682	655	203	96
<i>C</i>			90	48	1,010	210	210	1,249	857	342	?	?

A = amount found in 1:5 water extract, calculated to dry soil

B = same, calculated to water in soil at time of extraction

C = amount found in the displaced solution at same time

secondary salts. When the sum of the reaction values of all the ions in a solution is regarded as 100 and the percentage of the whole in primary and secondary salinity, and primary and secondary alkalinity is calculated, the relation between the composition of the water extracts and the displaced solutions is clear. With little exception, the water extracts have higher primary and lower secondary salinity than the displaced solutions. Concurrently, the water extracts have higher secondary alkalinity than the displaced solutions.

TABLE 2
Geochemical interpretation of the analyses

SOIL NUMBER	METHOD OF OBTAINING THE SOLUTION	SALINITY		ALKALINITY	
		Primary	Secondary	Primary	Secondary
18	Extracted	71.4	21.8	0.0	6.8
	Displaced	52.8	44.8	0.0	2.4
19	Extracted	83.6	0.0	14.4	3.0
	Displaced	70.4	17.6	10.0	2.0
20	Extracted	88.8	0.0	9.2	1.9
	Displaced	92.0	4.4	0.0	3.3
K	Extracted	62.8	18.8	5.6	17.4
	Displaced	49.4	38.4	0.0	11.8
Imperial	Extracted	80.6	4.2	0.0	16.2
	Displaced	52.8	43.2	0.0	3.2
R	Extracted	94.4	0.0	0.8	4.1
	Displaced	92.0	6.5	0.0	1.5
Colusa	Extracted	78.8	15.2	0.0	7.0
	Displaced	69.0	28.6	0.8	2.2
S1	Extracted	52.6	43.1	0.0	3.7
	Displaced	29.4	67.9	0.0	3.4
S2	Extracted	32.3	0.0	61.3	6.4
	Displaced	50.3	0.0	33.7	15.0

Secondary salinity is preferable to primary, in arable soils, therefore the picture presented by the water extract is less favorable than that given by the displaced solution. The actual condition in the soil is better than is indicated by the water extract. Secondary alkalinity is desirable, primary alkalinity very injurious to soil. In this respect, the displaced solution indicates that the actual condition in an alkali soil is worse than would be expected from an examination of the water extract. Thus the water extract considerably misrepresents the actual conditions in an alkali soil. But it will be observed that

the total alkalinity, sum of primary and secondary, is without exception, much less in the displaced solution. So, on the whole, the displaced solution gives a considerably better notion of actual conditions in the soil, and a much more favorable impression as to the suitability of the soil for the support of plant life. It seems probable that the larger proportion of calcium and magnesium in the true soil solution is due simply to the greater solubility of their salts in solutions of sodium salts, than in water alone.

Either method may be expected to reveal the principal defects of an alkali soil such as an excess of water soluble salts, or a low hydrogen-ion concentration whereby Ca, Mg, Fe and PO_4 are likely to be rendered unavailable to plants. One thing in which the displaced solution is decidedly superior is in the comparatively true representation of the actual concentration of solutes in the soil solution. The water extract will not give a correct impression unless the amounts found are calculated back to the concentration they would have in the actual soil moisture, and in the case of most of the ions, except Cl, NO_3 , and perhaps Na and K, this is likely to give a distorted picture of actual conditions.

SUMMARY

1. Nine different alkali soils have been examined by the two different methods, water extraction and displacement, and the analytical results on the two solutions compared.
2. The data indicate that the water extract does not represent the actual conditions in the soil. Carbonate, bicarbonate, and phosphate are greatly overestimated in the water extract. Chlorine, nitrate and sodium may be approximately correct, sulfate and potassium are much overestimated, and calcium and magnesium may be either high or low.
3. The actual concentration of solutes in the true soil solution may be much greater than is generally realized by one accustomed to thinking in terms of the amounts found in 1:5 water extracts.
4. The geochemical classification shows that the water extracts contain relatively larger proportions of sodium salts and less of calcium and magnesium salts than the true soil solution. The latter makes the soil appear more favorable for plant life than does the water extract method.

REFERENCES

- (1) BURD, J. S., AND MARTIN, J. C. 1923 Water displacement of soils and the soil solution. *In Jour. Agr. Sci.*, v. 13, p. 265-295.
- (2) HOAGLAND, D. R., MARTIN, J. C., STEWART, G. R. 1920 Relation of the soil solution to the soil extract. *In Jour. Agr. Res.*, v. 20, p. 381-395.
- (3) PALMER, CHASE 1911 Geochemical interpretation of water analyses. U. S. Geol. Sur. Bul. 479.
- (4) SCHREINER, OSWALD, AND FALLYER, GEORGE H. 1906 Colorimetric, turbidity, and titration methods used in soil investigations. U. S. Dept. Agr. Bur. Soils Bul. 31.

THE HYDROCHLORIC ACID METHOD FOR DETERMINING IN THE SOIL THE CATIONS PRESENT IN AN ABSORBED CONDITION

K. K. GEDROIZ

Liesnoi Institute, Petrograd

Received for publication August 29, 1923

A detailed method has been worked out for determining in the soil those cations which are present in the organic and mineral parts of the soil in an absorbed condition, by replacing them with the ammonium ion of ammonium chloride (1). This method is basic, since it doubtless gives the kind of cations present in the soil in an absorbed condition and their concentrations. But this method has its faults: It requires a considerable period of time, is expensive and the determination itself of the bases extracted from the soil by a solution of NH_4Cl represents certain difficulties due to the presence of large quantities of NH_4 in the solution.

The author's investigations (soon to be published) on the action of cold, dilute concentrations of hydrochloric acid upon the soil, suggest a simpler, more convenient and cheaper method. The method is based upon the fact that, on treating the soil with HCl not stronger than 0.05 N, there is an exchange of cations between the hydrochloric acid and the zeolitic-humic part of the soil, but not the formation of a solution.

The analysis is carried out as follows: 5-25 gm. of soil, depending on the abundance of absorbed bases in the soil and details of analysis, are treated in the cold with 25-50 cc. of 0.05 N HCl (exactness is not necessary here) in a small porcelain dish, and the suspension is then transferred upon a filter, (hardened paper no. 602) in a funnel, using the same acid; the soil is then washed with the same acid until the filtrate shows no trace of calcium. It is useless to make the test before about 300 cc. of filtrate is obtained. In making the test, one has to keep in mind that the HCl extracts some aluminum; it should, therefore, be carried out as follows: the filtrate is neutralized with ammonia, warmed to boiling, some oxalic acid is added until all the precipitated Al(OH)_3 is redissolved, then some ammonium oxalate is added.

The filtrate is treated as follows: it is evaporated to dryness on addition of some nitric acid, the organic matter is destroyed with aqua regia; the residue is dried for 30 minutes at 125-150°C., is dissolved in dilute HCl on warming and the SiO_3 is filtered off. To determine calcium and magnesium in the filtrate, the iron and aluminum have to be precipitated out; about 10 cc. of

1.0 N solution of NH_4Cl should be added to the liquid to make the filtration of the higher oxides. In determining the alkalies, the higher oxides and magnesium are separated by lime water. All these operations are carried out as soon as possible, since it is easy to contaminate the replaced bases by others.

There is basis to suppose that in soils greatly podsolized, where it seems that the formation of new absorbing complexes takes place in several horizons, the hydrochloric acid, even in the low concentration, may destroy to a certain extent this newly formed mineral-organic complex.

REFERENCES

- (1) GEDROIZ, K. 1918 On the method of determination of zeolitic bases in the soil. *In Zhur. Opt. Agron.*, v. 19, p. 226.

SOIL FLORA STUDIES

THOMAS L. MARTIN

Brigham Young University

Received for publication October 15, 1923

There are three distinct groups of organisms common to an ordinary soil which can readily be distinguished on gelatin plates. The names that have been applied to these groups are: actinomyces, non-spore-formers, and spore-formers. Much interesting information has already been gained concerning these organisms but there are still many things which need investigating. The author thought that some interesting data could be procured from a study of the effect, on the groups, of green manure at different stages of growth. The following experiment, therefore, was performed.

Rye, oats, and buckwheat were harvested at three different stages of growth, and cut into pieces about one inch in length. These pieces were incorporated with soil at the rate of five tons of green manure to the acre. The soil was then put into gallon pots filled with Dunkirk clay loam. Two series differing in decomposition periods were run. One was allowed to decompose for twelve months, the other for four months. The moisture content was kept at twenty-five per cent (dry basis) and a temperature of 28°C. was maintained in the green house during the whole experiment. After this incubation treatment, samples were taken and dilutions made at the rate of 1-100,000. All treatments were made in triplicate and for each pot triplicate gelatin plates were poured, thus giving nine poured plates of each manuring treatment. The medium was made with 1000 cc. tap water and 120 gm. of gelatin. The reaction of this medium was 0.005 N acid to phenolphthalein. The plates were incubated at 18°C. for 10 days. Counts were then made of the three groups of organisms, i.e., actinomyces, non-spore-formers, and spore-formers.

From the data presented it will be noted that:

1. The non-spore-formers are in a majority in a normal soil.
2. When green manures were added there were usually more total organisms.
3. In general the younger the manure added, the greater the numbers of actinomyces developed in proportion to other organisms.
4. Spore-formers were influenced proportionately less than the others.
5. The actinomyces group was influenced to the greatest extent.

These results seem to indicate that perhaps the particular function of the actinomyces group of organisms is that of cellulose decomposition.

Inasmuch as the three groups are constant for a normal soil,—and it appears that each outside influence has a specific effect upon the ratios of the groups,—perhaps a study of the effect of the numerous types of soil treatment may show as many different ratios. If so, this would aid in interpreting various soil phenomena or, at least, suggest a mode of attack in the solution of some of our soil problems.

TABLE 1
Organisms per gram of dry soil after treatment with rye as a green manure

STAGE OF GROWTH OF RYE	AVERAGE NUMBER OF ORGANISMS PER PLATE		
	Actinomycetes	Nonspore-formers	Spore-formers
<i>After twelve months humification</i>			
Check.....	1,900,000	2,000,000	300,000
Boot stage.....	2,371,200	2,918,400	729,600
Well headed.....	1,750,000	675,000	500,000
Almost ripe.....	1,200,000	650,000	300,000
<i>After four months humification</i>			
Fully headed.....	5,000,000	4,300,000	400,000
Heads turning yellow.....	3,200,000	1,900,000	500,000
Ripe.....	2,000,000	2,000,000	200,000

TABLE 2
Organisms per gram of dry soil after treatment with oats as a green manure

STAGE OF GROWTH OF OATS	AVERAGE NUMBER OF ORGANISMS PER PLATE		
	Actinomycetes	Nonspore-formers	Spore formers
<i>After twelve months humification</i>			
Check.....	1,900,000	2,000,000	300,000
Preceding boot stage.....	2,100,000	650,000	300,000
Late boot stage.....	1,800,000	450,000	260,000
Almost ripe.....	1,500,000	400,000	210,000
<i>After four months humification</i>			
Well headed.....	3,000,000	2,300,000	200,000
Turning yellow.....	2,700,000	1,700,000	300,000
Ripe.....	1,900,000	1,500,000	300,000

TABLE 3

Organisms per gram of dry soil after treatment with buckwheat as a green manure

STAGE OF GROWTH OF BUCKWHEAT	AVERAGE NUMBER OF ORGANISMS PER PLATE		
	Actinomyces	Nonspore-formers	Spore-formers
<i>After twelve months humification</i>			
Check.....	1,900,000	2,000,000	300,000
Just blossoming.....	3,800,000	900,000	450,000
Well blossomed.....	4,100,000	1,800,000	200,000
Just going to seed.....	3,500,000	1,650,000	175,000
<i>After four months humification</i>			
Well blossomed.....	4,000,000	2,100,000	100,000
Seeds forming.....	6,100,000	2,100,000	200,000
Ripe.....	3,100,000	2,000,000	200,000

STUDIES ON SULFUR OXIDATION IN OREGON SOILS

W. V. HALVERSEN AND W. B. BOLLEN

Oregon Agricultural Experiment Station

Received for publication September 18, 1923

INTRODUCTION

Sulfur applied as a fertilizer to certain soils in Oregon and elsewhere has greatly increased crop yields. Several types of soil in both southern and eastern Oregon show remarkable response to elemental as well as combined forms. Increases of 110 to 500 per cent in alfalfa yields are frequently obtained in these sections by comparatively light applications of either flour sulfur or gypsum. That several soil types in these same localities do not respond to sulfur fertilization is hardly less striking, especially in those instances where they are not only apparently similar to adjacent untreated responsive soils, but also practically the same in crop producing power.

The rôle of sulfur in soil fertility is a varied one. Primarily it is an essential plant food element but as such it is available to crops only in sulfate form. Sulfofication, or the oxidation of unavailable forms of sulfur to the available sulfate, results in the formation of sulfuric acid, which affects other constituents and processes of the soil. The accompanying increase in hydrogen-ion concentration also influences the soil as a culture medium, and, as demonstrated by a number of investigators advantage may be taken of this feature to control the potato scab fungus. Sulfur may thus have an indirect, as well as a direct fertilizing action on plant growth. In the instances cited herein its effect is not indirect, judging from evidence at hand.

HISTORICAL

Various sulfur fertilizers, as shown by Brown and Johnson (3) apparently stimulate ammonification in certain soils under laboratory conditions. This has been confirmed by Ames and Richmond (2) and by Ames (1) but these investigators found that in both acid and alkaline soils as ammonification was increased nitrate formation was decreased, the depression being less as acidity decreased and as basicity increased. They have also pointed out that increasing quantities of ammoniacal nitrogen which accompany decreasing amounts of nitrates when sulfur is oxidized cannot be considered as an indication of sulfofication with a stimulating effect on ammonification. The inverse relation between ammonia and nitrates is held to be due to a lack of sufficient basic material to neutralize the sulfuric acid produced in sulfofication, with the result that the ammonia unites with the acid and remains as ammonium sulfate instead of being nitrified. Since alfalfa and clover feed heavily on nitrate nitrogen, therefore thriving to best advantage on slightly alkaline soils, it is apparent that the action of sulfur on ammonification and nitrification is detrimental rather than favorable where these legumes are concerned.

Solvent action of the sulfuric acid produced in sulfur oxidation may increase soil fertility. That sulfification has a solvent action on unavailable phosphates has been shown by Lipman, McLean, and Lint (7). Nitrogen fixation, symbiotic and nonsymbiotic, may thus be indirectly stimulated; several investigators, notably Ashby, have pointed out that available phosphorus increases this soil function. According to Chauzit (4) the benefits obtained from sulfur fertilization on certain soils in France are due to its rendering soluble and readily assimilable the fertilizing elements of organic matter and some mineral substances. This action, however, varies with the quantity of sulfur applied and with the length of time of contact with the soil, best results having been obtained with 300 to 500 pounds of sulfur per acre applied as far as possible in advance of the time when the plants are most in need of nutritive elements.

REASONS FOR THIS INVESTIGATION

Where applications of only 100 pounds of sulfur per acre to Oregon soils give marked increases in yields over a period of three years, the solvent effect can be of little importance. This is further supported by the fact that response is noticeable within a few weeks after the sulfur is applied in the spring just previous to seeding. Either flour sulfur or gypsum is used in this manner with equal effectiveness. The use of gypsum which is not subject to sulfification eliminates any solvent action.

It would seem, therefore, that sulfur fertilizers act directly by supplying a limiting plant food element. This is to be suspected also from chemical analyses, which show that the responsive soils are comparatively low in total sulfur, the amounts ranging from 0.006 to 0.024 per cent. The location of these soils precludes any appreciable factors affecting their sulfur content. Not only is the rain-fall light, averaging 17 inches per year in the Medford area, 13 inches in Klamath Falls vicinity, and 8 inches in the Columbia basin region, but it is also relatively low in sulfur content since the regions are sparsely settled and practically free from coal smoke. For the same reason the irrigation water, which comes from melting snow on surrounding mountains, is likewise probably low in sulfur.

Reasons for no response from sulfur fertilizers when applied to certain soils may be several. The soil may contain an ample supply of sulfates, in which case if a low crop-producing power exists there must be some other limiting factor. If a soil responds to sulfate fertilizers but not to elemental sulfur, it is evident that conditions for sulfification are unfavorable.

Since sulfification is largely a microbiological process, primarily a function of certain soil bacteria and fungi, any differences in its extent may be due to variations in physiological efficiency or to relative numbers of the micro-organisms involved. On this basis inoculated sulfur or sulfur composts containing bacteria of high sulfur-oxidizing efficiency would be of great economic value. In general farm practice an application of this material would be desirable on soils low in available sulfur and low in sulfur-oxidizing efficiency. Its need under Oregon field conditions would be indicated only on soils which respond to sulfates but not to unavailable forms of sulfur.

Variations in physiological efficiency, or in relative numbers of sulfotifying organisms, can be ascribed to environmental factors, of which the total sulfur supply in the soil may be important. It is reasonable to suppose that a deficiency of sulfur would at least reduce the number of obligate sulfotifiers, probably reduce the numbers of facultative sulfotifiers, and also reduce their efficiency as the stimulus for maximum activity would be lacking. An ample sulfur supply, on the other hand, would furnish food for a maximum number of sulfotifying microorganisms and enable them to develop their highest efficiency, other conditions being favorable.

The depth and physical condition of the soil must be taken into account, however, when considering the relation of sulfur supply to crop yields. Two soils may show on analysis the same percentage of sulfur but while one may respond to the application of sulfur the other may not solely because of a difference in depth or physical condition. This has been emphasized by Reimer (9), who pointed out that a deep mellow soil provides new feeding areas for plant roots several years after a shallower soil has become exhausted, and that sulfification is probably able to proceed more rapidly in mellow soils because of better aeration.

PLAN OF INVESTIGATION

To determine any relation that certain factors connected with sulfur supply and sulfur transformation in a soil may have to response obtained from sulfur fertilization, the investigation herein reported was conducted. The specific aims in view were the following:

1. To determine the sulfotifying power of representative soil types and to find if this power is low or lacking in types not responding to sulfur fertilization.
2. To find a relation between total sulfur content and sulfotifying power.
3. To find a relation between sulfotifying power and sulfate content.
4. To find a relation between total sulfur content and sulfate content.
5. To find if any relation exists between the hydrogen-ion concentration and the sulfotifying power of the soil.
6. To find any relation existing between the sulfur oxidizing power and the buffer value of the soil.
7. To correlate if possible any relation between the texture of the soil and its buffer value.

COLLECTION OF SAMPLES

Samples of fourteen soil types representative of four distinct areas of Oregon were obtained for study. Except for two samples obtained locally, these were collected and sent in by persons other than the investigator. Clean cement bags were supplied as shipping containers and proper instructions for collection were given to insure representative samples free from undue contamination.

Samples from the irrigated Columbia basin district were sent in by H. K. Dean, superintendent, Umatilla branch experiment station. Southern Oregon samples were furnished by F. C. Reimer, superintendent, Southern

Oregon branch experiment station. F. H. Thomas, county agent for Klamath County, submitted the central Oregon samples. A muck sample, representative of a large area in Marion County, was obtained through C. V. Ruzek, professor of soil fertility, Oregon Agricultural College, and two other Willamette Valley samples were collected on the college farms. A description of the various samples follows.

COLUMBIA BASIN SOILS

1. *Umatilla station, check plot.* Medium sandy soil, which, being light and arid, is naturally deficient in organic matter and plant food. Rotations and feeding of crops on the land are necessary to maintain and increase fertility. Sample taken from a field which has produced alfalfa for ten years.

2. *Umatilla station, sulfured plot.* Same as sample 1 except that sulfur at the rate of 100 pounds per acre was applied in March, 1919, resulting in no increase in yield of alfalfa.

3. *Stanfield project, check plot.* Fine sandy soil of same origin as sample 1 to which it is apparently similar in all characters other than texture. It also has produced alfalfa for ten years.

4. *Stanfield project, sulfured plot.* Same as sample 3 but sulfured at the rate of 100 pounds per acre in March, 1919. A large increase in yield of alfalfa resulted.

SOUTHERN OREGON SOILS

5. *Salem clay loam, check plot.* A deep, fertile, clay loam containing 21 per cent of clay and 40 per cent of silt. Though distinct from adobe it becomes sticky when wet and hard when dry. The potassium, calcium, and magnesium content is high. The nitrogen supply is fair in the surface soil but low in the subsoil. The amount of phosphorus and sulfur present is low. Alfalfa grown on this soil has a pale, yellowish-green color, and the growth is so poor that weeds often outgrow the alfalfa.

6. *Salem clay loam, sulfured plot.* Same as sample 5 but has received two applications of sulfur at the rate of 100 pounds per acre, the first in 1915 and the second in March, 1917. The response to sulfur was remarkable. The alfalfa became a dark, rich green color, grew luxuriantly, and was practically free from weeds.

7. *Medford loam, check plot.* This soil is a deep, fertile, brown silt loam well supplied with potassium, calcium, magnesium and nitrogen. The phosphorus content is low. There is also a deficiency of sulfur. No response has been obtained from any sulfur fertilizer on this soil type.

8. *Antelope clay adobe, check plot.* This is a deep and well drained heavy, black, adobe soil. It has a high water-holding capacity and is of a sticky nature. In late summer it becomes dry and hard and checks badly. Potassium, calcium, magnesium, organic matter and limestone are present in abundance. The content of phosphorus and sulfur is low. Alfalfa grown on this soil has a pale yellowish color and grows poorly. This crop responded rapidly to sulfur fertilizers with greatly increased yields and a rich, dark green color in the vegetation.

CENTRAL OREGON (KLAMATH COUNTY) SOILS

9. *Altamont ranch, check.* Fine sandy loam taken from a field where no sulfur has been applied. Sulfur applied to adjacent fields has not produced noticeable results.

10. *Case ranch, check.* Fine sandy loam soil which would probably respond to sulfur judging from increased yields obtained with sulfur on neighboring fields.

11. *Case ranch, sulfured.* Fine sandy loam located near sample 10. Sulfured two years ago at the rate of 100 pounds per acre. Alfalfa yields were increased by the treatment.

WILLAMETTE VALLEY SOILS

12. *Willamette silt loam, check plot.* Brown silt loam soil, well drained, acid in character. It is well supplied with calcium nitrogen, potassium, and phosphorus, and has a fair content of sulfur. Sulfur has been used as a fertilizer on this soil type. The field from which the sample was taken has produced one crop of vetch and oats and one crop of corn. No fertilizers have been applied.

13. *Dayton silt loam, check plot.* A gray soil on stiff, gray and yellow mottled subsoil with poor drainage. Calcium, nitrogen, and potassium are present in ample amounts, but there is a deficiency of both sulfur and phosphorus. Noticeable results are obtained from top dressings of gypsum on clover, 40 to 80 pounds being the usual rate of application per acre. The plot sampled has grown vetch and oats two years and has been top dressed twice with gypsum at the rate of 80 pounds per acre.

14. *Muck.* This soil is high in organic matter and nitrogen content. Sulfur, and calcium are abundant but phosphorus and potassium are low and often limiting factors. Sulfur is not used as a fertilizer on this type, although it is carried in superphosphate, which is frequently used in amounts as high as 500 pounds per acre as a source of phosphorus. The field from which the sample was taken is devoted exclusively to the production of onions.

METHODS

As soon as the samples were received at the laboratory they were air dried, passed through a 10-mesh sieve, and stored in two- and four-gallon glazed stoneware crocks fitted with cardboard covers.

Optimum moisture content for all incubation studies was taken as 50 per cent saturation.

Sulfofication. The sulfofying power of each soil was tested by adding sodium sulfide or sulfur to duplicate 100-gm. portions of soil and determining the amount converted to sulfate within a definite period of time, 7-14 days. In some tests 100 mgm. of flour sulfur were used while in others one cubic centimeter of a 10 per cent sodium sulfide solution was used. At the close of the incubation period the soils were tested quantitatively for sulfates by the turbidity method of Schreiner and Faileyer (10, p. 54).

Clarification of soil extracts. After water digestion all the soils except the heavy clays gave filtrates more or less yellow in color. Since this color interfered with the turbidity determination for sulfates a means for its removal was imperative.

Bone black was first tried and 2 or 3 gm. of the chemically pure powder was added to the filtrate, which, after thorough agitation, was filtered through a Gooch crucible. This was fairly successful but with the more highly colored solutions the treatment had to be repeated several times to remove the color entirely.

The use of aluminum hydroxide was suggested by the method employed by Emerson (5) for clearing soil extracts for nitrate determinations. A suspension of the hydroxide was prepared from alum according to Emerson's directions but the hydroxide could not be washed entirely free from sulfate. Accordingly, 100 gm. chemically pure aluminum chloride was dissolved in a liter of distilled water and concentrated ammonium hydroxide was then added until precipitation was complete. The precipitate was allowed to concentrate, after which it was transferred to a 3-liter flask and washed three times with 2-liter portions of distilled water, the wash water being decanted after the hydroxide had concentrated to about 1 liter. After the third washing 1 liter of distilled water was added and the pH value adjusted to approximately 7.2 with standard hydrochloric acid. Another liter of distilled water was then added, making three liters of the suspension for use.

Of the thoroughly shaken hydroxide suspension thus prepared, amounts varying from 10 to 20 cc. according to the soil were found to insure colorless filtrates in all cases except with muck, when added to the solutions either at the beginning of digestion or just previous to filtering. Filtrates from muck were readily clarified with 30 cc. of suspension, but amounts up to 60 cc. added before filtering would not give an entirely colorless filtrate.

Total sulfur. The total sulfur content of each soil was determined by fusion with sodium peroxide in an illium bomb (Parr sulfur bomb). This method has the advantage of requiring much less time than fusion in an open crucible, but considerable difficulty was encountered in securing a satisfactory routine and the lack of agreement obtained between duplicates leaves something to be desired. It is probable, however, that had more time been devoted to a study of variations in routine it could have been made to yield results entirely satisfactory. Notwithstanding variations of as much as 20 per cent between duplicates the data may be considered comparative and as serving the purpose of this investigation.

Blank determinations were made to obtain a correction factor for the sulfur in the chemicals used in making up a charge.

Hydrogen-ion concentration. The hydrogen-ion concentration was determined by the colorimetric method. The solutions to be tested were secured by agitating 100 gm. of the soil with 200 cc. of distilled water and removing the soil particles by filtering through filter paper or a Chamberland filter.

TABLE 1
Oxidation of sodium sulfide

SOIL NUMBER	SOIL TYPE	MOISTURE REQUIRED FOR SATURATION per cent air-dry wt.	SULFUR AS Na ₂ S OXIDIZED	
			In 7 days	In 14 days
1	Medium sand.....	28.1	26	19
2	Medium sand.....	29.7	26	21
3	Fine sand.....	25.9	27	23
4	Fine sand.....	29.4	18	21
5	Clay loam	38.7	3	11
6	Clay loam.....	40.7	15	20
7	Loam.....	31.1	10	23
8	Clay adobe.....	52.6	4	8
9	Sandy loam.....	41.4	25	17
10	Sandy loam.....	37.6	16	16
11	Sandy loam.....	40.9	20	18
12	Silt loam.....	50.0	2	30
13	Silt loam.....	40.1	4	8
14	Muck	225.5	26	..

RESULTS

Oxidation of sodium sulfide. That the water-holding capacity is in inverse ratio with the sulfur-oxidizing power on soils of low organic content is a general conclusion that seems apparent from table 1 and figure 1. This does not hold true for the muck soil 14. Since most Oregon soils are of the semi-arid type and naturally low in organic content this conclusion becomes more significant.

All soils tested showed considerable efficiency in oxidizing sodium sulfide. A greater yield of sulfates was secured in the coarser textured soils. More sulfate was found at the end of seven than at the end of fourteen days in the light sandy soils. It is quite probable that these soils contain very little

buffer hence the hydrogen-ion concentration would soon become strong enough to retard oxidation and possibly favor the development of sulfate consuming organisms.

Sulfurization of flour sulfur vs. inoculated sulfur. The normal Oregon field application of sulfur is 100 pounds per acre. This is applied as long as possible before the crop is planted. In some semi-arid sections county agents are

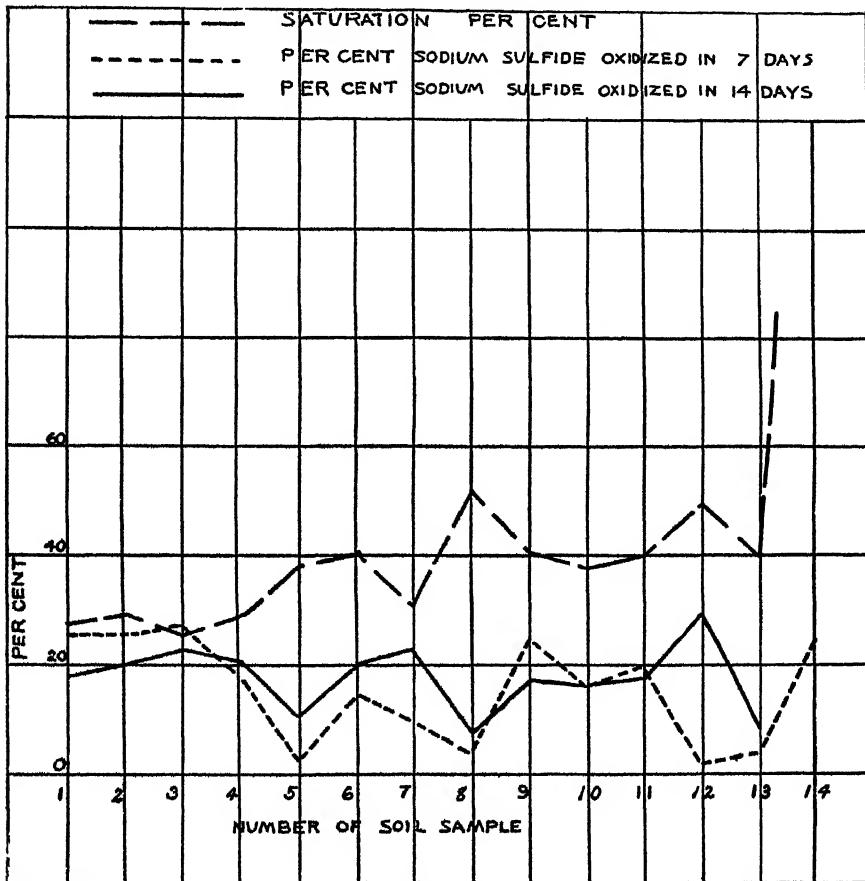


FIG. 1. WATER-HOLDING CAPACITY AND SULFUR OXIDATION

recommending that it be applied in the fall so as to be available for the growing season in the following spring. Under these extensive cropping conditions the fact that a limiting plant food element is being supplied is our great consideration, the control of potato scab and liberation of phosphorus and potassium being of secondary consideration.

Since preliminary tests are showing that even under humid conditions, sulfur is giving some remarkable increases in yield, it becomes of value to determine the rapidity with which the sulfur is oxidized, so as to know how

long before planting the sulfur must be applied. Much waste of soluble sulfates might thus be eliminated. It is under such conditions that a readily oxidizable source of sulfur would prove of greatest value.

The inoculated sulfur tested was supplied through the courtesy of Dr. J. G. Lipman, director of the New Jersey agricultural experiment station. This material seems to be effective in stimulating sulfur oxidation and in several cases it was more completely oxidized than was flour sulfur by the same soil. It is evident that the relative oxidizing powers are not altered by inoculated sulfur.

Table 3 and figure 2 give a comparison between the total sulfur content, the sulfate content and the sulfur-oxidizing efficiency. The total sulfur analyses show that all soils except the muck soil 14 are low in total sulfur.

TABLE 2
Sulfocification of flour sulfur vs. inoculated sulfur

SOIL NUMBER	SULFATES				AMOUNT OXIDIZED	
	Start*	Check	Flour sulfur	Inoculated sulfur	Flour sulfur per cent	Inoculated sulfur per cent
			g p.m.	g p.m.		
1	15	50	1140	1032	36	33
2	22	68	1596	1200	51	38
3	27	52	876	1128	28	36
4	56	336	1848	2256	50	64
5	26	44	276	312	8	9
6	36	52	408	540	12	17
7	18	54	432	480	13	14
8	30	64	156	180	3	4
9	76	194	648	888	15	23
10	47	74	444	840	12	26
11	94	119	708	1176	23	35
12	496	648	948	948	10	10
13	25	34	100	140	2	4
14	239	444	2280	1876	61	48

* Sulfates in soil used for sulfocification test.

The figures given are averages of triplicate determinations. No apparent relation exists between the total sulfur content and the sulfur-oxidizing power. An interesting fact is that the field application of sulfur to Umatilla sandy soil 2, and Stanfield fine sand 4, had little or no effect on the total sulfur content yet the sulfur-oxidizing power was stimulated by making the soil a favorable medium for the growth of the sulfur oxidizing bacteria. The sulfate content was higher in soil 4. This soil is not subject to extensive leaching like soil 2. In comparing soils 5 and 6, Salem clay loam, it will be seen that the field application of sulfur caused only a slight increase in the sulfur-oxidizing power and that the total sulfur and the sulfate content were not affected. This soil gave a remarkable increase in the yield of alfalfa when 100 pounds of sulfur was applied in 1915. This plot was sulfured again in 1917. Despite the low sulfur content of soil 7 (Medford loam) this soil has failed to show

to lack of sulfur bacteria. Antelope clay adobe (soil 8) always gives an enormous increase in the yield of alfalfa when sulfur is applied at 100 pounds per acre, yet the total sulfur is higher than the Medford loam and the sulfur-oxidizing power is less.

The fine sandy loam soils of Klamath County vary widely in their total sulfur content. Soil 9 was taken from an unsulfured area where no crop response to sulfur was apparent. This may be explained by the high sulfur content. Samples 10 and 11 from the Case ranch show little variation. The application of sulfur stimulated the sulfur-oxidizing power of soil 11 despite the lower total sulfur content.

The Willamette Valley soils 12 (Willamette silt loam) and 13 (Dayton silt loam) have a comparatively high total sulfur content and a low sulfur-oxidizing power. The low sulfur-oxidizing power especially in the Dayton silt loam is due to the fact that the soils are heavy, and it seems apparent that aeration

TABLE 3
Relation between total sulfur, sulfate content and sulfur oxidizing power

SOIL NUMBER	TOTAL SULFUR		SULFATE CONTENT parts per million	SULFUR OXIDIZED IN 14 DAYS per cent
	parts per million	per cent		
1	55	0.006	14	28
2	55	0.006	18	39
3	145	0.015	21	21
4	110	0.011	115	38
5	155	0.016	25	7
6	135	0.014	23	10
7	80	0.008	18	11
8	110	0.011	24	2
9	235	0.024	64	11
10	144	0.014	42	9
11	110	0.011	94	16
12	274	0.028	526	7
13	164	0.016	21	2
14	780	0.078	296	36

is one of the most essential factors to sulfur oxidation. Sample 14 (muck) has a high sulfur-oxidizing power and a high total sulfur and sulfate content.

THE BUFFER VALUES OF THE SAMPLES STUDIED

Recently an article by Joffe and McLean (6) reported work along somewhat similar lines. The samples of soil used by them came from the southern Oregon region and with one exception were heavy soils. Some of these same soil types are used in this experiment along with soils of varying physical and chemical composition from three other regions. With the exception of samples 12, 13 and 14 these soils all came from semi-arid irrigated sections.

The sulfur used in this experiment was equivalent to one ton per acre. That this amount is excessive can easily be deduced from the previous mention that 100 pounds of sulfur per acre gives an increase of several hundred per cent on some of these soils when applied to alfalfa.

the original reaction and the reaction after four weeks of incubation. These soils are irrigated with water coming from mountains containing limestone and various salts of high buffer qualities which remove the possibility of any injurious accumulation of acids through the oxidation of nominal amounts of sulfur.

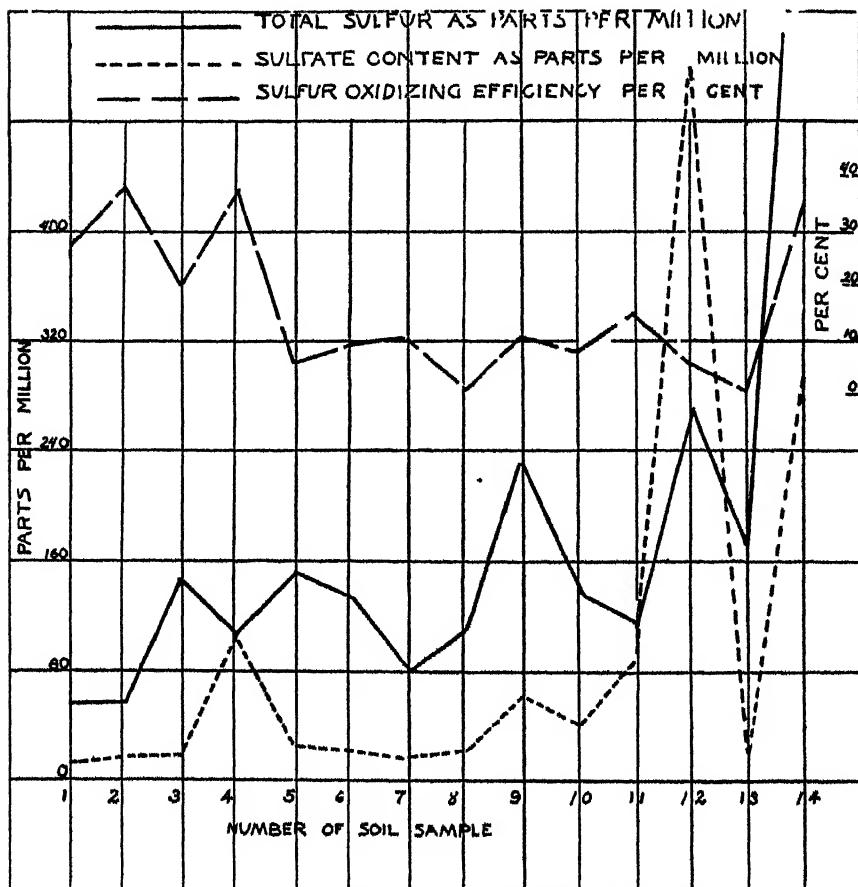


FIG. 2. SULFUR, SULFATES AND SULFUR-OXIDIZING POWER

Table 4 also points to the fact that inoculated sulfur is oxidized more rapidly than uninoculated sulfur. Since the value of sulfur when applied to alfalfa in Oregon lies in the fact that a limiting plant food element is being supplied and that all soils studied have a strong oxidizing flora, our data does not show any appreciable margin between the commercial values of the two forms.

There are slight discrepancies in the data presented in regard to reaction as well as to the yield of sulfates. This is to be expected. Variations in the compactness of the soils in the tumblers and wide experimental factors in the

TABLE 4
Buffer qualities of soils studied

SAMPLE NUMBER	TYPE OF SOIL	ORIGINAL REACTION	INCUBATED 1 MONTH				INCUBATED 2 MONTHS				INCUBATED 4 MONTHS			
			Flour sulfur*		Inoculated sulfur*		Flour sulfur*		Inoculated sulfur*		Flour sulfur*		Inoculated sulfur*	
			pH	Reaction	SO ₄ per 100 gm. soil	pH	Reaction	SO ₄ per 100 gm. soil	pH	Reaction	SO ₄ per 100 gm. soil	pH	Reaction	SO ₄ per 100 gm. soil
1	Medium sand	7.2	6.0	57.1	6.0	100.0	6.2	100.0	5.4	80.0	5.0	261.0	5.0	375.0
2	Medium sand	7.0	6.2	111.3	5.9	107.7	5.4	160.0	5.1	89.0	5.0	400.0	4.6	400.0
3	Fine sand	7.1	6.0	76.9	5.9	66.7	5.8	80.0	5.9	80.0	4.6	300.0	4.6	500.0
4	Fine sand	6.8	6.0	83.3	5.9	105.2	5.4	123.0	5.2	89.0	4.9	400.0	4.9	428.0
5	Clay loam	6.4	6.0	66.7	5.9	100.0	6.4	89.0	5.9	89.0	5.5	333.5	5.5	400.0
6	Clay loam	6.8	6.2	58.8	5.9	74.1	6.4	89.0	5.9	133.3	5	222.0	5.8	300.0
7	Loam	6.9	6.4	66.7	5.8	74.1	6.0	42.1	6.2	160.0	5	500.0	5.6	222.0
8	Clay adobe	6.7	6.6	26.2	5.9	43.5	6.8	45.7	6.6	80.0	6.2	286.0	6.4	318.0
9	Sandy loam	6.2	6.1	41.2	5.9	47.1	6.4	40.0	6.0	48.8				
10	Sandy loam	6.4	6.2	33.2	6.0	57.2	6.4	40.0	5.9	84.3	5.6	272.5	5.8	300.0
11	Sandy loam	6.4	6.4	100.0	5.5	107.7	6.6	177.8	6.3	84.3	5.2	375.0	5.8	400.0
12	Silt loam	5.6	5.6	33.2	5.6	55.6	5.9	57.2	5.9	67.7	5.8	127.7	5.4	333.5
13	Silt loam	5.8	5.9	28.6	5.9	6.2	5.9	32.7	6.2	29.6	5.0	158.0	4.8	153.7
14	Muck	5.4	5.8	46.0	5.6	52.2	5.8	57.2	5.4	37.6	5.2	120.0	5.2	160.0

*One hundred grams of sulfur used to each 100 gm. of soil in a glass tumbler.

CONCLUSIONS

1. All soils included in the investigation are capable of oxidizing sodium sulfide and flour sulfur. While there is considerable variation between soils in sulfur oxidizing efficiency all appear to be efficient enough to oxidize enough sulfur to supply the needs of starving plants within a comparatively short time.
2. A general relation exists between sulfofying power and sulfate content, curves representing these running more or less parallel.
3. No relation is apparent between total sulfur content and sulfofying power.
4. No relation exists between total sulfur content and sulfate content.
5. Application of sulfur to a soil tends to increase the sulfur oxidizing efficiency of that soil.
6. Inoculated sulfur stimulates sulfofication, but for the soils studied its need is not indicated.
7. Temperature and aeration are important factors affecting sulfofication, an increase in either tending to increase the rate of sulfur oxidation.
8. The buffer qualities of the soils studied are indicated by their change in hydrogen-ion concentration. The heavy soils show a remarkable ability to neutralize the acidity formed through the oxidation of sulfur. The soils

studied having high buffer value were heavy soils in which sulfur oxidation was slow compared to the light sandy soils of low buffer value.

9. No apparent relationship exists between the hydrogen-ion concentration and the sulfur oxidizing power of a soil.

REFERENCES¹

- (1) AMES, J. W. 1921 Solvent action of nitrification and sulfification. Ohio Agr. Exp. Sta. Bul. 351.
- (2) AMES, J. W., AND RICHMOND, T. E. 1918 Sulfification in relation to nitrogen transformations. *In* Soil Sci., v. 5, no. 4, p. 311-321.
- (3) BROWN, P. E., AND JOHNSON, H. W. 1916 Studies in sulfification. Iowa Agr. Exp. Sta. Res. Bul. 34.
- (4) CHAUZIT, J. 1921 Fertilizing action of sulfur. *In* Bul. de l'Academie d'Agriculture, v. 7, no. 21, p. 472-493.
- (5) EMERSON, PAUL. 1921 The colorimetric determination of soil in a colored water extract. *In* Soil Sci., v. 12, no. 5, p. 413-417.
- (6) JOFFE, J. S., AND MCLEAN, H. C. 1922 A note on oxidation of sulfur in Oregon soils. *In* Soil Sci., v. 14, no. 3, p. 217-221.
- (7) LIPMAN, J. G., MCLEAN, H. C., AND LINT, H. CLAY. 1916 Sulfur oxidation in soils and its effect on the availability of mineral phosphates. *In* Soil Sci., v. 2, no. 6, p. 499-538.
- (8) LIPMAN, J. G., WAKSMAN, S. A., AND JOFFE, J. S. 1921 The oxidation of sulfur by soil microorganisms: I. *In* Soil Sci., v. 12, no. 6, p. 475-489.
- (9) REIMER, F. C., AND TARTAR, H. V. 1919 Sulfur as a fertilizer for alfalfa in southern Oregon. Ore. Exp. Sta. Bul. 163.
- (10) SCHREINER, O., AND FAILYER, G. H. 1906 Colorimetric, turbidity, and titration methods used in soil investigations. U. S. Dept. Agr. Bur. Soils Bul. 31.

INDEX

- Abbott, Ernest V. (paper), The Occurrence and Action of Fungi in Soils, 207-216
Acid phosphate, effect of, on liberation of soil potassium, 395-397
Actinomycetes, effect of partial sterilization of soils on, 353
Alfalfa—
A Preliminary Study of the Effect of Sodium Chloride upon, Grown in Solution Cultures (paper), S. Lomanitz, 183-192
Effect of Sulfur, Calcium and Phosphorus on the Yield and Composition of, on Six Types of Idaho Soils (paper), Ray E. Neidig, G. R. McDole and H. P. Magnuson, 127-136
Alkali Soil, The Leaching of (paper), J. E. Greaves, C. T. Hirst and Yeppa Lund, 407-426
Ammonification, studies on, with fungi, 209-210
Auten, J. T. (paper), Organic Phosphorus of Soils, 281-294

Bacteria—
effect of toluene and heat treatment on numbers of, in soils, 151-154, 353-356
spore formers and non-spore formers as affected by partial sterilization, 353-354
Bicarbonates—
equilibrium studies of sodium, and carbonate, 295-320
extraction of, from alkali soils, 467
Blair, A. W., and Prince, A. L. (paper), The Influence of the Nitrogen Treatment on the Content of Nitrogen, Carbon and Phosphoric Acid in a Soil Varying in Mechanical Composition, 115-119
Bollen, W. B., Halversen, W. V., and (paper), Studies on Sulfur Oxidation in Oregon Soils, 479-490
Buffer values of some Oregon soils, 487-488

Calcic additions, effect of, on sulfate outgo from soil 1-40, 159-182
Calcic and Magnesic Additions, The Influence of, upon the Outgo of Sulfates from a Loam Soil as Measured by Lysimeter Leachings over an 8-year Period (paper), W. H. MacIntire, W. M. Shaw and J. B. Young, 1-40
Calcium—
comparison of, found by the displacement and water extract method, 466
effect of—
absorption of, by plants, 228, 233-234
on liberation of soil potassium, 217-223
on yield and composition of alfalfa, 127-136
outgo of, from lysimeter tanks, 322-332, 450-462
removal of, in leachings of variously treated alkali soils, 416-419
Calcium carbonate—
effect of—
on biological activities of soil, 253-254
on outgo of calcium from lysimeters, 330
on outgo of magnesium from lysimeters, 334, 336
Calcium oxide—
effect of—
on biological activities in soil, 251-253, 344-350
on leachings in lysimeter studies, 322, 332
Carbonates, equilibrium studies of sodium, and bicarbonates, 295-320
Carbon bisulfide—
effect of, on biological activities of soil, 263-267
Carbon dioxide—
influence of various treatment on production of, in soil, 267
in sterilized soils, 402-405
liberation of, in relation to availability of potassium, 398-405
Carleton, Everett A. (paper), Comparison of the Jones Calcium Acetate Method for Lime Requirement with the Hydrogen-ion-Concentration of Some Quebec Soils, 79-90

- Chlorine—**
 absorption of, by plants, 232-233
 effect of sodium chloride on, of alfalfa, 189
- Chlorosis, the, of pineapple plants grown on manganeseiferous soils, 269-274**
- Culture solution—**
 comparison of the growth of plants in, and in soils, 370-377
 effect of—
 different volumes of, on plant growth, 367-370
 sodium chloride upon alfalfa grown in, 183-192
 expressing the composition of, 384
 phosphates in, as compared with those in soil solution, 379-380
- Dolomite—**
 effect of—
 on liberation of soil potassium, 217-223
 on outgo of calcium from lysimeters, 331
 on outgo of magnesium from lysimeters, 336-337
 on outgo of sulfates from soil, 1 40
- Feldspars, liberation of potassium from, 390-406**
- Ferrous sulfate—**
 effect of, on calcium and magnesium leachings, 452-455, 457-458
 effect of, on outgo of sulfates in soil, 152-189
- Fertilizer treatment, response of soils to, 442-446**
- Fieger, Ernest A., Rost, Clayton O., and (paper), Effect of Drying and Storage upon the Hydrogen-ion Concentration of Soil Samples, 121 126**
- Fungi—**
 effect of, on solubility of rock phosphate, 210 211, 214
 effect of toluene and heat treatment on number of, in soil, 151-154, 352-353
 sulfur oxidized by, 212-214
- The Occurrence and Action of, in Soils (paper), Ernest V. Abbott, 207-216**
- Gedroiz, K. K. (paper), The Hydrochloric Acid Method for Determining in the Soil the Cations Present in an Absorbed Condition, 473-474**
- Greaves, J. E., Hirst, C. T. and Lund Yewpa (paper), The Leaching of Alkali Soil, 407-426**
- Gypsum, effect of, on water soluble potassium, 134-135**
- Halverson, W. V. and Bollen, W. B. (paper), Study on Sulfur Oxidation in Oregon Soils, 470 190**
- Heat, effect of, on bacteria, fungi and accumulation of soluble nitrogen in soil, 151-154**
- Hibbard, P. L. (paper), Comparison of the Soil Solution by Displacement Method and the Water Extract of Alkali Soils, 465-471**
- Hirst, C. T., Greaves, J. E. and Lund Yewpa (paper), The Leaching of Alkali Soil, 407 426**
- Hoagland, D. R. (paper), The Absorption of Ions by Plants, 225 246**
- Hoagland, D. R. and Martin, J. C. (paper), A Comparison of Sand and Solution Cultures with Soils as Media for Plant Growth, 367 388**
- Hydrochloric acid method for determining absorbed cations in soil, 473 474**
- Hydrogen-ion concentration—**
 and litmus test for soil reaction, 91-94
 and soil moisture influencing development of potato scab, 69 73
 colorimetric and electrometric determination of, in soil extract, 83 90
 effect of, on liberation of soil potassium, 394
 in relation to plant distribution, 48 49
 in relation to root distribution, 50 53
 in relation to sulfur oxidation in soils, 488-489
- of culture solutions with alfalfa grown in such solution, 189 190**
- of Soil Samples, Effect of Drying and Storage upon the (paper), Clayton O. Rost and Ernest A. Fieger, 121 126**
- of Some Quebec Soils, A Comparison of the Jones Method for Lime Requirement with the (paper), Everett A. Carleton, 79-90**
- of subsoil, 41-48**
- relation of soil depth to, 41-54**
- Iron—**
 availability of—
 and plant growth, 370
 in manganeseiferous soils, 273

- Johnson, Harlan W. (paper), A New Apparatus for Mechanical Analysis of Soils, 363-366
- Jones method for determining lime requirement as compared with the hydrogen-ion-concentration method, 79-90
- Kelley, Arthur Pierson (paper), Soil Acidity, an Ecological Factor, 41-54
soils and methods of testing, 41-48
relation to root distribution, 48-49
plant distribution, 50-53
- Lime, effect of, on water soluble potassium, 134-135, 217-223
- Lime requirement, a comparison of Jones calcium acetate method with the hydrogen-ion concentration, 79-90
- Litmus Method for Detecting the Soil Reaction, The (paper), Everett A. Carleton, 91-94
- Lomanitz, S. (paper), A Preliminary Study of the Effects of Sodium Chloride upon Alfalfa Grown in Solution Cultures, 183-192
- Lund Yewpa, Greaves, J. E., Hirst, C. T. and (paper), The Leaching of Alkali Soil, 407-426
- Lysimeter—
studies on the outgo and retention of calcium and magnesium, 322-341, 450-462
sulfates in leachings, 1-40
- Lysimeters, The Effect of Plants on the Concentration of Drainage Water from the Cornell (paper), Benjamin D. Wilson, 427-432
- MacIntire, W. H., Shaw, W. M. and Young, J. B. (paper), A 5-year Lysimeter Study of the Supposed Liberation of Soil Potassium by Calcic and Magnesic Addition, 217-223
- MacIntire, W. H., Shaw, W. M. and Young, J. B. (paper), Influence of Calcic and Magnesic Treatments upon Sulfate Leachings from Soil Alone and with Additions of Ferrous Sulfate, Pyrite and Sulfur, 159-182
- MacIntire, W. H., Shaw, W. M. and Young, J. B. (paper), Reciprocal Repression Exerted by Calcic and Magnesic Addi-
- tions upon the Solubility of Native Materials in Surface Soil, 449-464
- MacIntire, W. H., Shaw, W. M. and Young, J. B. (paper), The Influence of Calcic and Magnesic Additions upon the outgo of Sulfates from a Loam Soil as Measured by Lysimeter Leachings over an 8-year Period, 1-40
- MacIntire, W. H., Shaw, W. M. and Young, J. B. (paper), The Variant Roles of Soil and Subsoil in Calcium-Magnesium Interchange, 321-341
- Magnesite—
effect of—
on calcium outgo from lysimeters, 331
on magnesium outgo from lysimeters, 337
on sulfate outgo from soils, 1-40
- Magnesium—
absorption of, by plants, 228
effect of, on liberation of soil potassium, 217-223
extractions by various methods, 466
outgo of, from lysimeter tanks, 332-338, 450-462
removal of, in leachings of variously treated alkali soils, 416-419
- Magnesium carbonate—
effect of, on outgo of calcium from lysimeters, 330
effect of, on outgo of magnesium from lysimeters, 335
- Magnesium oxide—
effect of, on outgo of calcium from lysimeters, 322-330
effect of, on outgo of magnesium from lysimeters, 332-334, 450-462
- Magnuson, H. P., Neidig, Ray E., McDole, G. R. and (paper), Effect of Sulfur, Calcium and Phosphorus on the Yield and Composition of Alfalfa on Six Types of Idaho Soils, 127-136
- Magnuson, Harry P., Neidig, Ray E. and (paper), Equilibrium Studies of Sodium Carbonates and Bicarbonates in some Idaho Soils, 295-320
- Martin, J. C., Hoagland, D. R. and (paper), A Comparison of Sand and Solution Cultures with Soils as Media for Plant Growth, 367-388
- Martin, Thomas L. (paper), Soil Flora Studies, 475-477

- Martin, Wm. II (paper), Influence of Soil Moisture and Acidity on the Development of Potato Scab, 69-73
- McCool, M. M., Veatch, J. O. and Spurway, C. H. (paper), Soil Profile Studies in Michigan, 95-106
- McDole, G. R., Neidig, Ray E. and Magnuson, H. P. (paper), Effect of Sulfur, Calcium and Phosphorus on the Yield and Composition of Alfalfa on Six Types of Idaho Soils, 127-136
- McGeorge, W. T. (paper), Acidity of Highly Basic Soils, 195-206
- McGeorge, W. T. (paper), The Chlorosis of Pineapple Plants Grown on Manganiferous Soils, 269-274
- McHargue, J. S. (paper), Convenient Supports for Plants in Pot or Water Culture Experiments, 359-360
- Millar, C. E. (paper), Studies on Virgin and Depleted Soil, 433-448
- Moisture—
effect of, on soil color, 275-279
Influence of Soil, and Acidity on the Development of Potato Scab (paper), Wm. II. Martin, 69-73
- Morse, F. W. (paper), Comparative Effect of Muriate and Sulfate of Potash on the Soil in a Long Continued Fertilizer Experiment, 107-114
- Neidig, Ray E. and Magnuson, Harry P. (paper), Equilibrium Studies of Sodium Carbonates and Bicarbonates in Some Idaho Soils, 295-320
- Neidig, Ray E., McDole, G. R. and Magnuson, H. P. (paper), Effect of Sulfur, Calcium and Phosphorus on the Yield and Composition of Alfalfa on Six Types of Idaho Soils, 127-136
- Nitrates—
absorption of, by plants, 228
extraction of, from alkali soils, 467
in cropped and uncropped soils, 430-432
- Nitrification as an index of soil fertility, 55-67
- Nitrogen—
content of fertilized and unfertilized soils, 116
determinations as a criterion of the crop producing power of soil, 117
effect of sodium chloride on, of alfalfa, 189
- removal of, in leachings of variously treated alkali soils, 421-422
- O'Neal, A. M. (paper), The Effect of Moisture on Soil Color, 275-279
- Organic matter—
effect of, on solubility of cropped and virgin soils, 439-440
influence of, on biological activities in soils, 266
- Parker, F. W. and Tidmore, J. W. (paper), A Modification on the Truog Soil Acidity Test, 75-78
- Phosphorus—
absorption of, by plants, 233
effect of—
fungi on solubility of, 210-211
on yield and composition of alfalfa, 127-136
organic, of oil, 281-294
removal of, in leachings of variously treated alkali oil, 419-420
- Phosphate extraction by various methods, 467
- Plant distribution as related to soil acidity, 41-54
- Plant growth, a comparison of sand and solution cultures with soil as a media for, 367-388
- Plant nutrients, loss of, in drainage of alkali soils, 423-424
- Plants—
Absorption of Ions by (paper), D. R. Hoagland, 225-246
comparison of the growth of, in solution cultures, sand and soils, 370-377
- Convenient Support for, in Pot or Water Culture Experiments (paper), J. S. McHargue, 359-360
- the effect of, on the concentration of drainage water from lysimeters, 427-432
- Potash, Muriate and Sulfate of, Comparative Effect of, on the Soil in a Long Continued Fertilizer Experiment, (paper), F. W. Morse, 107-114
- Potassium—
Absorption of, by plants, 228, 231
A 5-year Lysimeter Study of the Supposed Liberation of Soil, by Calcic and Magnesic Additions (paper), W. H.

- MacIntire, W. M. Shaw and J. B. Young, 217-223
effect of manure extract on liberation of soil, 390-391
removal of, in leachings of variously treated alkali soils, 420-421
The Liberation of, from Feldspars and of Potassium and Carbon Dioxide from Soils by Fertilizer and Acid Treatment (paper), S. C. Vandecayeye, 389-406
water soluble, as affected by lime, lime and sulfur, gypsum and sulfur alone in soil, 134-135
- Prince, A. L., Blair, A. W. and (paper), The Influence of the Nitrogen Treatment on the Content of Nitrogen, Carbon and Phosphoric Acid in a Soil Varying in Mechanical Composition, 115-119
- Protozoa, influence of soil treatment on activities of, 250
- Pyrite, effect of—
on calcium and magnesium leachings, 454-455, 458-460
on sulfate outgo of soils, 152-189
- Rost, Clayton O. and Fieger, Ernest A. (paper), Effect of Drying and Storage upon the Hydrogen-ion Concentration of Soil Samples, 121-126
- Sand Cultures, a comparison of, and solution cultures with soils as media for plant growth, 367-388
- Serpentine—
effect of—
on outgo of calcium from lysimeters, 331
on outgo of magnesium from lysimeters, 337-338
on outgo of sulfates from soil, 1-40
- Shaw, W. M., MacIntire, W. H. and Young, J. B. (paper), A 5-Year Lysimeter Study of the Supposed Liberation of Soil Potassium by Calcic and Magnesic Additions, 217-223
- Shaw, W. M., MacIntire, W. H. and Young, J. B. (paper), Influence of Calcic and Magnesic Treatments upon Sulfate Leachings from Soil Alone and with Additions of Ferrous Sulfate, Pyrite and Sulfur, 159-182
- Shaw, W. M., MacIntire, W. H. and Young, J. B. (paper), Reciprocal Repression Exerted by Calcic and Magnesic Additions upon the Solubility of Native Materials in Surface Soil, 449-464
- Shaw, W. M., MacIntire, W. H. and Young, J. B. (paper), The Influence of Calcic and Magnesic Additions upon the Outgo of Sulfates from a Loam Soil as Measured by Lysimeter Leachings over an 8-Year Period, 1-40
- Shaw, W. M., MacIntire, W. H. and Young, J. B. (paper), The Variant Roles of Soil and Subsoil in Calcium-Magnesium Interchange, 321-341
- Sodium—
absorption of, by plants, 231
carbonate, effect of, on leachings and structure of alkali soils, 409-425
Carbonates and Bicarbonates, Equilibrium Studies of, in Some Idaho Soils. (paper), Ray E. Neidig and Harry P. Magnuson, 295-320
- Sodium chloride, effect of, on alfalfa grown in culture solutions, 183-192
effect of, on leachings and structure of alkali soils, 409-425
- Sodium Sulfate, effect of, on leachings and structure of alkali soils, 409-425
- Soil—
air drying of, influence of, on biological activities, 254-258
alkali, methods of reclaiming, 407
Color, Effect of Moisture on (paper), A. M. O'Neal, 275-279
Flora Studies (paper), Thomas L. Martin, 475-477
heating of, influence of, on biological activities, 258-260
lime requirement of, as determined by the Jones and hydrogen-ion concentration method, 79-90
moisture, influence of, on development of potato scab, 69-73
Microbiological Analyses of, as an Index of Soil Fertility. IV. Nitrification (paper), Selman A. Waksman, 55-67
- Partial Sterilization of, Microbiological Activities and Soil Fertility, I. (paper), Selman A. Waksman and Robert L. Starkey, 137-156, II. 247-268, III. 343-357

- Profile Studies in Michigan (paper), M. M. McCool, J. O. Veatch and C. H. Spurway, 95-106
- Reciprocal Repression Exerted by Calcic and Magnesic Additions upon the Solubility of Native Materials in Surface Soil, W. H. MacIntire, W. M. Shaw, and J. B. Young, 449-464
- The Hydrochloric Acid Method for Determining in the, the Cations Present in an Absorbed Condition (paper), K. K. Gedroiz, 473-474
- the litmus tests for detection of reaction of, 91-94
- The Variant Roles of, and Subsoil in Calcium-Magnesium Interchange (paper), W. H. MacIntire, W. M. Shaw and J. B. Young, 321-341
- types, as related to hydrogen-ion concentration, 41-54
- Soil Acidity—**
- an Ecological Factor (paper), Arthur Pierson
 - Influence of, on development of potato scab, 69-73
 - modification of Truog, test, 75-78
 - of highly basic soils, 195-206
- Soils—**
- absorption phenomena of sodium carbonate in, 315-318
 - A Comparison of Sand and Solution Cultures with, as Media for Plant Growth (paper), D. R. Hoagland and J. C. Martin, 367-388
 - A New Apparatus for Mechanical Analysis of (paper), Harlan W. Johnson, 363-366
 - Manganiferous, the Chlorosis of Pineapple Plants grown on (paper), W. T. McGeorge, 269-274
 - Organic Phosphorus of (paper), J. T. Auten, 281-294
 - response of, to fertilizer treatment, 442-446
 - Studies on Depleted and Virgin (paper), C. E. Millar, 433-448
 - Soil Solution—**
 - Comparison of the, by Displacement Method and the Water Extract of Alkaline Soils (paper), P. L. Hibbard, 465-471
 - in its physiological aspects, 377-379
 - in virgin and depleted soils, 433-443
- Starkey, Robert L., Wakeman, Selman A. and (paper), Partial Sterilization of Soil, Microbiological Activities and Soil Fertility I, 137-156
- Starkey, Robert L., Wakeman, Selman A. and (paper), Partial Sterilization of and Soil, Microbiological Activities and Soil Fertility, II, 247-268, III, 343-357
- Subsoil, acidity in, 41-48
- Sulfates—**
- absorption of, by plants, 230-232
 - effect of calcic and magnesic additions on outgo of, 1-40, 159-182
 - extraction of, from alkali soils, 467
 - of potash, their effect on cumulative chemical properties of soils, 107-114
- Sulfur—**
- effect of—
 - on biological activities of soil, 266
 - on calcium and magnesium leachings, 450-451, 457-458
 - on outgo of sulfates from soil, 152-189
 - on water soluble potassium, 134-135
 - on yield and comparison of alfalfa, 127-136
 - inoculated versus uninoculated, 487-488
 - oxidation by fungi, 212-214
- Studies on, Oxidation in Oregon Soils, (paper), W. V. Halverson and W. B. Bollen, 479-490
- Spurway, C. H., McCool, M. M., Veatch, J. O. and (paper), Soil Profile Studies in Michigan, 95-106
- Tidmore, J. W., Parker, F. W. and (paper), A Modification of the Truog Soil Acidity Test, 75-78
- Tillering, effect of sand and solution cultures on, 375-377
- Toluene—
- effect of, on bacterial numbers in soil, 151-154
 - on biological activities of soil, 261-263, 344-350
- Truog Soil Acidity Test, Modification of, (paper), F. W. Parker and J. W. Tidmore, 75-78
- Vandecaveye, S. C. (paper), The Liberation of Potassium from Feldspars, and of Potassium and Carbon Dioxide from Soils by Fertilizer and Acid Treatment, 389-406

- Veatch, J. O., McCool, M. M. and Spurway, C. H. (paper), Soil Profile Studies in Michigan, 95-106
- Waksman, Selman A. (paper), Microbiological Analysis of Soil as an Index of Soil Fertility, VI, Nitrification, 55-67
- Waksman, Selman A. and Starkey, Robert L. (paper), Partial Sterilization of Soil, Microbiological Activities and Soil Fertility, II, 247-268, III, 343-357
- Waksman, Selman A. and Starkey, Robert L. (paper), Partial Sterilization of Soil, Microbiological Activities and Soil Fertility, I, 137-156
- Wilson, Benjamin D. (paper), The Effect of Plants on the Concentration of Drainage Water from the Cornell Lysimeters, 427-432
- Wollastonite—
effect of—
calcium from lysimeters, 331
magnesium from lysimeter, 337-338
on outgo of, sulfates from soil, 1-40
- Young, J. B., MacIntire, W. H., Shaw, W. M. and (paper), A 5-Year Lysimeter Study of the Supposed Liberation of Soil Potassium by Calcic and Magnesic Additions, 217-223
- Young, J. B., MacIntire, W. H., Shaw, W. M. and (paper), Influence of Calcic and Magnesic Treatments upon Sulfate Leachings from Soil Alone and With Additions of Ferrous Sulfate, Pyrite and Sulfur, 159-182
- Young, J. B., MacIntire, W. H., Shaw, W. M. and (paper), Reciprocal Repression Exerted by Calcic and Magnesic Additions upon the Solubility of Native Materials in Surface Soil, 449-464
- Young, J. B., MacIntire, W. H., Shaw, W. M. and (paper), The Influence of Calcic and Magnesic Additions upon the Outgo of Sulfates from a Loam Soil as Measured by Lysimeter Leachings over an 8-Year Period, 1-40
- Young, J. B., MacIntire, W. H., Shaw, W. M. and (paper), The Variant Roles of Soil and Subsoil in Calcium-Magnesium Interchange, 321-341

